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CARBON-CARBON COMPOSITE MATRIX REACTIONS AND DENSIFICATION RESP--ETC(U)
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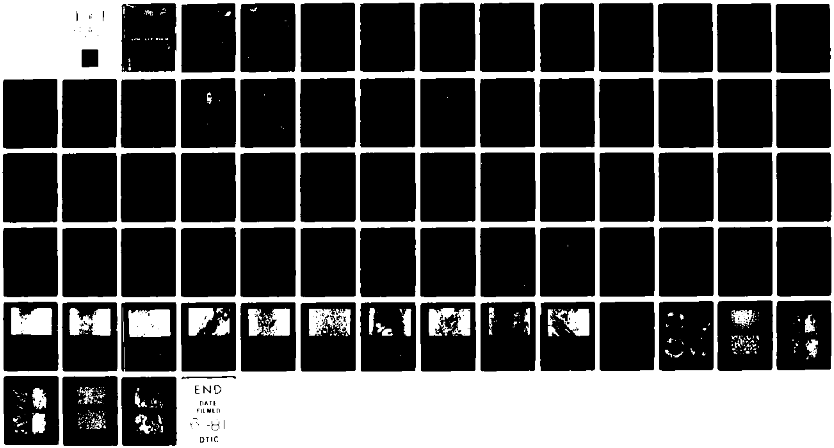

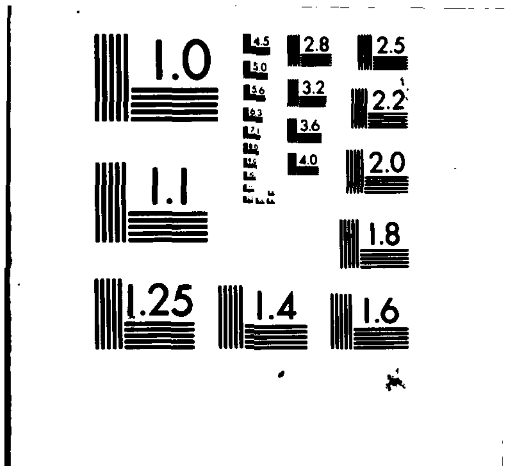


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SCIENCE APPLICATIONS, INC.

(12)

CARBON-CARBON COMPOSITE MATRIX
REACTIONS AND DENSIFICATION RESPONSE

Contract No. 49620-78-C-0002
& F49620-79-0068

Air Force Office of Scientific Research (AFOSR)
Bolling Air Force Base, Washington, D.C. 20332



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FINAL TECHNICAL REPORT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A mini-Hot Isostatic Pressure (HIP) autoclave has been fitted with internal and external diagnostic apparatus for monitoring decomposition rates and events of pressure-temperature-time scheduled carbonization of coal tar pitch. TGA's high pressure liquid chromatography, gel permeation and compositional analysis techniques have been used to parametrically study critical events of coal tar pitch carbonization.

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## FORWARD

This report was prepared by the Material Sciences Operation (MSO) of Science Applications, Inc. (SAI), Irvine, California for the Air Force Office of Scientific Research (AFOSR), Bolling Air Force Base, Washington, D.C. under Contract Nos. F49620-78-C-0002 and F49620-79-C-0068. It is a final report documenting the work conducted from November 1, 1977 to January 14, 1980 on the program entitled "Carbon-Carbon Composite Matrix Reactions and Densification Response." The Air Force project monitor for this program was Dr. Donald R. Ulrich. His guidance and contributions are gratefully acknowledged.

Mr. J.P. Pope was the MSO/SAI Program Manager and Principal Investigator for this effort. Principal contributors to the program and this report are S. Coley, specimen fabrication and J.J. Glatz who completed the program when Mr. Pope left MSO/SAI.

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CARBON-CARBON COMPOSITE MATRIX REACTIONS
AND DENSIFICATION RESPONSE

Contract Nos. F49620-78-C-0002 & F49620-79-C-0068

## I. INTRODUCTION

Carbon-carbon composites have become the baseline high temperature material for selected critical components of advanced Air Force launch and reentry systems. Carbon-carbon is now being used by the Air Force in Integral Throat and Entrance (ITE) rocket nozzles, exit cones and combined clear air and aggravated encounter reentry nosetips. Because of the critical nature of these components there is concern regarding the reliability and reproducability of the carbon-carbon processing technology base. The complex processing environment can be described in the most general terms as severe, stochastic and agressively damaging. It is often a more severe environment than the component experiences during its design function. The phenomena of the process environment governing the formation of constituent properties and final composite attributes are poorly understood. Existing models are, in most cases, a correlation of post-process properties and carbon-carbon microstructure to imposed external parameters of the process cycle and supposed internal events (which are unsupported by internal diagnostic information). These models have been developed from a decade of empirical experimentation by processors at several facilities with a variation of equipment, materials and process parameters.

The development of basic information about the constituents of carbon-carbon material and their behavior during impregnation and carbonization cycles will provide the basis for development of an accurate model of the

changes that occur in the manufacturing process. With this understanding the critical process parameters can be identified and controlled with a more uniform product as the end result. A better understanding of the critical coal tar pitch precursor parameters may develop into the use of other low cost precursors.

## II. OBJECTIVES

The objective of this program was to provide some information on the basic thermochemical characteristics of coal tar pitch, the thermal and pressure parameters that significantly modify the properties, and on the reproducability of the material. This information was obtained by conducting unique and innovative processing experiments.

## III. SUMMARY OF WORK

A small research Hot Isostatic Pressure (HIP) autoclave was purchased with Science Applications, Incorporated (SAI) funds for use in this program. The research vessel, an Autoclave Engineers, Inc. hot wall vessel is rated for reaction pressures up to 15,000 psi and 700°C internal temperatures and has experimental load dimensions of 3 inch diameter by 10 inch length. Using SAI Corporate funds, the HIP unit was modified to a Material Sciences Operation (MSO/SAI) design by Conaway Pressure Systems, Inc. (CPSI), Columbus, Ohio. The modification included providing access to the internal regions for the installation of diagnostic equipment to monitor thermal and thermochemical events during processing, and for real time analysis of gaseous effluents emanating from the decomposition of coal tar pitch.

Due to schedule and technical problems at CPSI, the modified research

HIP facility was not returned until August 1978. Further technical problems with the unit delayed operational status until late September 1978. Since then, decomposition reactions have been studied at 3000, 5000, 10,000, and 15,000 psi imposed carbonization pressures on Allied Chemical CP 277-15V coal tar pitch. Carbonization cycles based upon the Air Force's Equivalent Industrial Standard Process (EISP) have been conducted for the full time-temperature-pressure schedule as well as for process runs interrupted in the liquid-solid transformation temperature range of the pressure decomposition of coal tar pitch (450°-490°C).

A technique for the hot recovery of liquid pitch from these interrupted runs was developed. This procedure provides material for the determination of properties and chemical and compositional changes of previously unmeasured pitch conditions of the process environment. These material property measurements of pitch recovered at or near 470°C have provided significant information regarding chemical and compositional variances between the still liquid state and transformed solid forms of pitch.

Characterization of basic compositional and chemical differences were made between manufacturing dates of lots of Allied 15V pitch, between samples within the same lot, and between the Allied material and Koppers Chemical, Incorporated's version of the Air Force's 15V specifications. The effect of preconditioning the precursor before impregnation has been studied and a correlation between heat treatment time and mesophase formation was derived.

The use of High Pressure Liquid Chromatography (HPLC), and Gel Permeation (GP) techniques to resolve compositional and chemical structural

differences between precursors and partially processed liquid states of pitch was implemented. Analysis of the HPLC and GP data were compared to thermogravimetric analysis data to establish key features of the pitch precursors which respond distinctively to process parameters.

Fiber studies in which Hercules HM yarns (PAN) and Union Carbide VSB-32 pitch yarns are included in the decomposition experimental packages were done. Significant structural changes in fully carbonized yarns impregnated with Allied 15V were observed as a result of processing according to an EISP schedule at 10,000 and 15,000 psi. Yarns included in runs interrupted at 470°C and rapidly quenched were strikingly different from fully carbonized yarns processed at the same pressure. Comparative measurements of yarn bundle specimen HIPped normally and with interrupted processing were made. The results showed that the pitch fibers were modified whereas the HM fibers were not significantly changed.

Other important results include the discovery of a large concentration of hydrogen in pitch removed from EISP processed pitch at 10,000 and 15,000 psi carbonization pressures. Similarly, material recovered from interrupted runs showed that only minor reduction in the hydrogen content of Allied 15V had occurred by 470°C in contrast to calculated equilibrium decomposition rates. At the same time, the oxygen weight content of recovered material is significantly higher than the precursor in material removed from the carbonization runs interrupted at 470°C, and higher yet for fully carbonized (EISP) material.

Pitch samples carbonized at 5,000 and 10,000 psi were tested in flexure

to determine the influence of pressure on the pitch strength. The difference in processing pressure was not a strong influence but the vertical location of the specimen in the can did significantly effect the mechanical properties. The carbonized pitch ultimate strength and elastic modulus increased by approximately a factor of 3 between specimens taken from the bottom and top of the carbonization containers. The pitch density also increased from the bottom to the top of the container.

## IV. DESCRIPTION OF WORK

### 1. Experimental Approach

The research approach was based upon completeness of precursor characterization and unique experimental packages and analysis techniques. Early in the program, it was recognized that the contribution of this program to the Air Force's Processing Science objectives could best be met by expanding the data base to include pitch precursors from different vendors and manufacturing dates as well as including experimental pitches which may be of interest to the Air Force over the next decade. For this reason, the program was expanded to include Koppers Chemical, Inc. pitches such as their 15V Equivalent of the Allied 15V baseline material and several experimental pitches. Although not planned for study until 1979, the Koppers pitches were integrated into the processing and characterization phases in late 1978 to provide additional data for resolution of compositional issues.

Midway through the first year's effort, it became apparent that additional chemical analysis techniques were required to completely characterize pitch precursors and to model the thermophysical and thermochemical response of pitch material to imposed pressure and temperature schedules. For this

reason, two techniques, high pressure liquid chromatography and gel permeation were incorporated into the measurement methods. Results obtained on various pitches and conditions of the same pitch material that were received in later 1978 and early 1979 are reported later in this section.

Table 1 presents a summary of the experimental approach to the research effort. Table 2 is a presentation of the pitch material which was obtained for this program.

2. Equipment and Experimental Package Designs

The basic equipment used in conducting decomposition reaction experiments is shown schematically in Figure 1. The research HIP facility was modified to provide access to the inner region of the autoclave for introduction of diagnostic apparatus for monitoring on a real time basis, the events and thermal profiles of decomposing pitch. External monitoring of input power and heat transfer is also continuously recorded to provide for evaluation of the heat conduction of the reacting mass in the load. The modification to the HIP vessel was based upon requirements to measure variables of the process environment as shown in Figure 2. Experimental packages were designed uniquely for isolation of precursor response to imposed process parameters. Figure 3 shows schematically a typical experimental package for the research HIP facility and the types of process parameters and package variables employed. Figure 4 is a reproduction of the recorded history of a typical decomposition run.

3. Coal Tar Pitch Characterizations

The basic composition and decomposition characteristics of Allied 15V,

Table 1

REACTION STUDIES

| MATRIX TYPE | CONDITION AND EFFECT | TECHNIQUES | OBSERVABLES/MEASUREMENTS |
|---|---|---|---|
| Allied-15V<br>Lot-501<br>Lot-701<br>Koppers "15V Equivalent"<br>Koppers KCP<br>Koppers Exp. Pitches | As Received<br>Heat Treatment<br>. Time<br>. Temperature<br>. Mechanical Agitation<br>. Bubble Percolation<br>Carbonization Cycle<br>. Heat Rate<br>. Pressure<br>. Temperature<br>. Modified Loads<br>- Pore Volume<br>- Surface Area<br>. Interrupted Runs | Microscopy<br>Chemical Analysis<br>TGA/Derivaties<br>Bulk Physical Properties<br>. Post Heat Treatment<br>Experimental Packages | • Temp. Dependent Viscosity<br>• Softening Point<br>• Benzene Insolubles<br>• Quinoline Insolubles<br>• Temp. Dependent Weight Loss<br>• Temp. Dependent Decomposition Rates<br>• Hydrogen/Carbon Ratio<br>• Bulk & Apparent Density<br>• Mesophase Formation<br>• Pitch Density/Porosity<br>. Bulk<br>. Apparent<br>• Surface/Volume Effect on Impregnation Efficiency<br>• Pyrolysis Gas Rates<br>• High Pressure Liquid Chromatography<br>• Gel Permeation |

Table 2

PITCH MATERIALS TO BE INVESTIGATED

| IMPREGNATING PITCH | MANUFACTURING DATE | SOFTENING POINT, °C (1) |
|---|---|---|
| Allied 15V - Lot 501 | 1975 | 85° |
| Allied 15V - Lot 701 | 1977 | 93° |
| Koppers "15V Equivalent" | 1977 | 95° |
| Koppers "15V Equivalent" 3275-1 | 1978 | N/A |
| Koppers KCP Impregnating Pitch | 1978 | 115° |
| Koppers Experimental Pitch/78-252-524 | 1978 | 110°-120° (2) |
| Koppers Experimental Pitch/78-524 | 1978 | 110°-120° (2) |
| Koppers Carbon Impregnating Pitch Y/78-480 | 1978 | 110°-120° (2) |

(1) As determined by SAI
(2) Telecon: Koppers/SAI

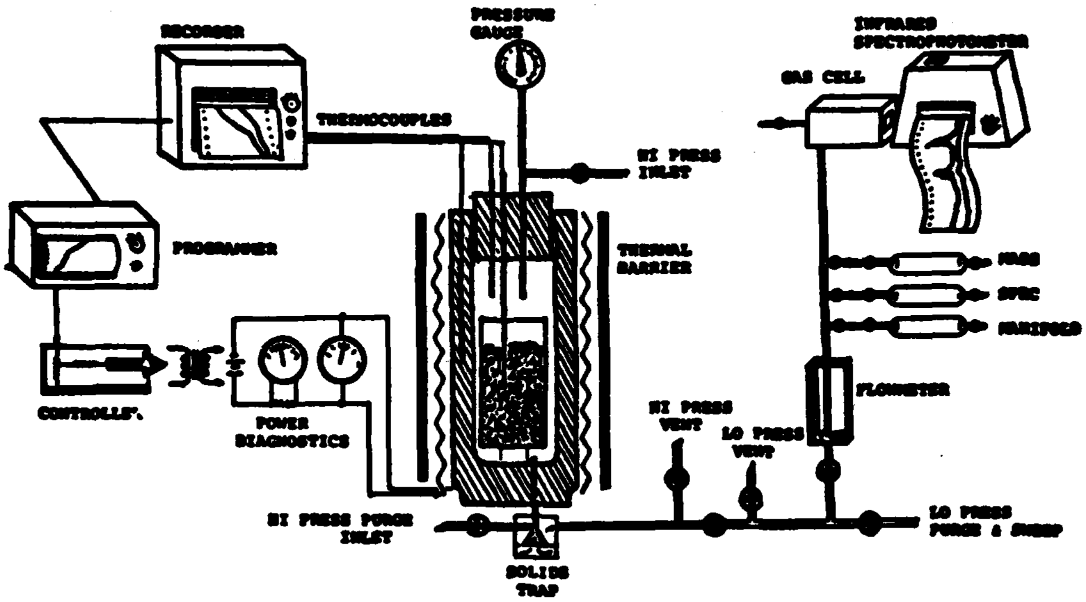

Figure 1. Schematic of Research HIP Facility

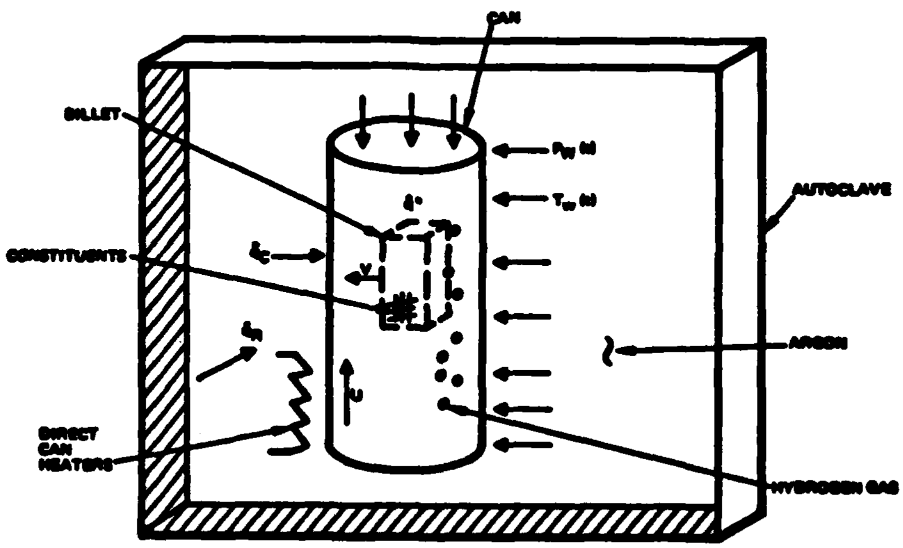

Figure 2. Process Environment Model

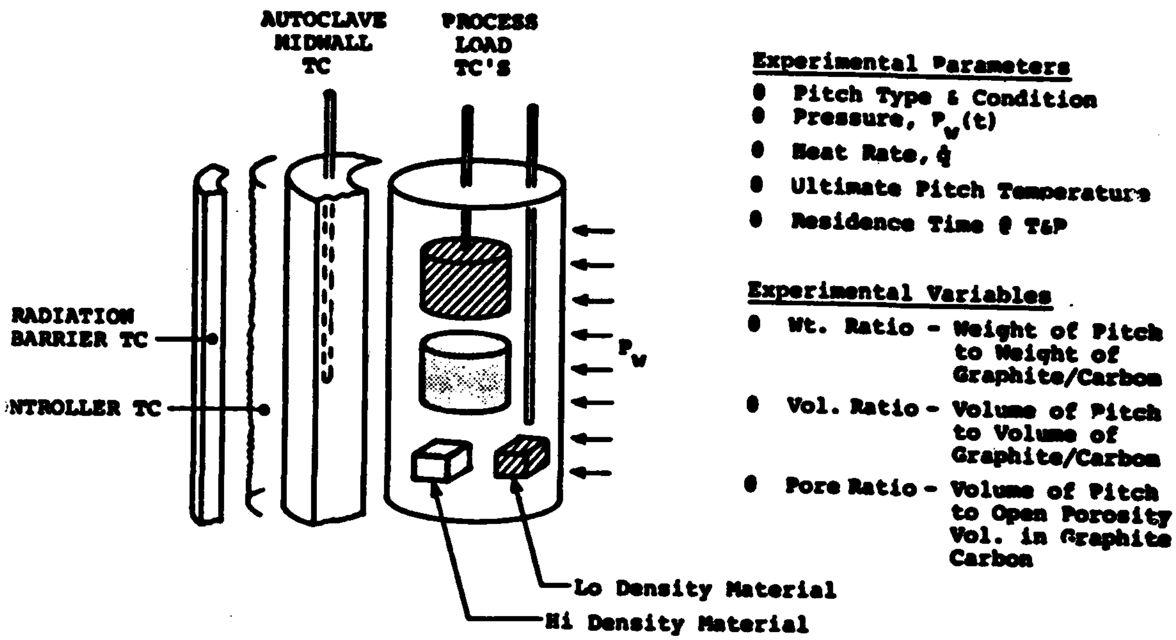


Figure 3. Schematic of Typical Experimental Package

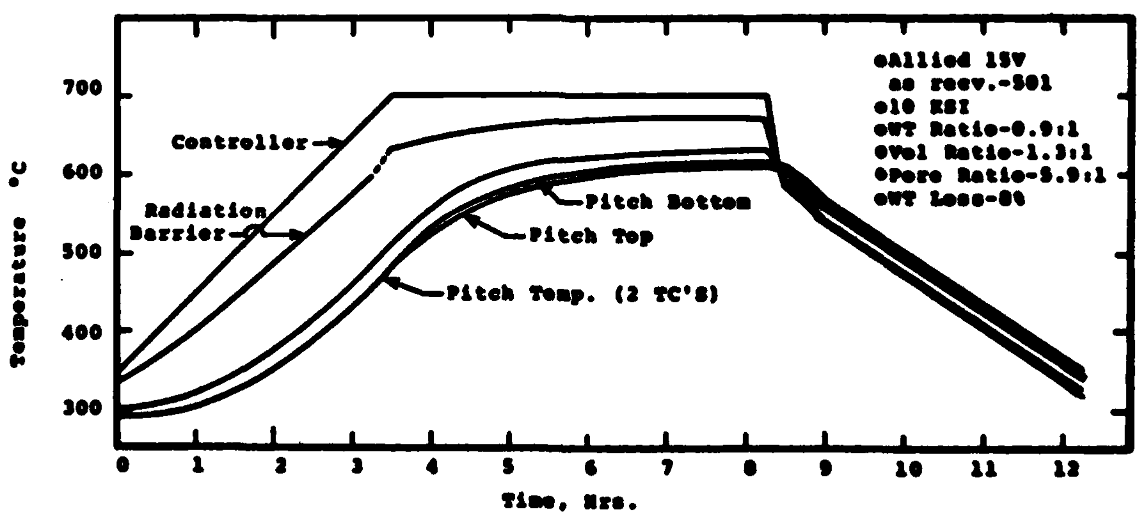


Figure 4. Reproduction of Recorded History of 10 KSI Carbonization Reaction Experiment

Koppers 15V, and two experimental impregnating pitches obtained from Koppers are presented in Table 3, and Figures 6 through 16. Included in that data are the variation in properties and composition of lots of Allied 15V manufactured in 1975 and 1977 (Lot 501 and Lot 701, respectively). Three barrels from each lot were analyzed for chemical elements of the composition, benzene and quinoline insolubles (B.I. and Q.I.), softening point, and ash content (Table 3). A significant increase in the average of the oxygen content was determined for Lot 701 along with increases in B.I. and Q.I. content and softening point. The significance of these changes on the decomposition reactions was not determined. However, the increase in oxygen content of the precursor pitch material is of specific interest because of measured increases in the oxygen content of fully carbonized pitch to be discussed in Paragraph 4.

Table 3

PROPERTIES OF ALLIED 15V FOR TWO
MANUFACTURING DATES (AVERAGE OF THREE DRUMS PER LOT)

| LOT NO. | MFG. DATE | SOFT. PT. °C | VISCOSITY @ 200°C CENTIPOSIE | B.I. W/O | Q.I. W/O | ELEMENTAL COMPOSITION, W/O C | H | N | S | O | Ash |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 501 | 1975 | 87.5 | 27.0 | 14.50 | 2.50 | 92.42 | 4.83 | 1.07 | 0.53 | 1.03 | 0.15 |
| 701 | 1977 | 91.1 | 47.5 | 17.74 | 4.05 | 91.49 | 4.53 | 1.03 | 0.61 | 2.23 | 0.10 |

Important compositional difference between Lot 501 and Lot 701 (Allied 15V) are shown in the gel permeation data of Figure 5, and the TGA data of Figures 6 and 7. Of particular interest is the apparent shift of distribution and increase in total complex molecular compounds found in Lot 701 when compared to the earlier manufacturing date of Lot 501 (Figure 5). At the

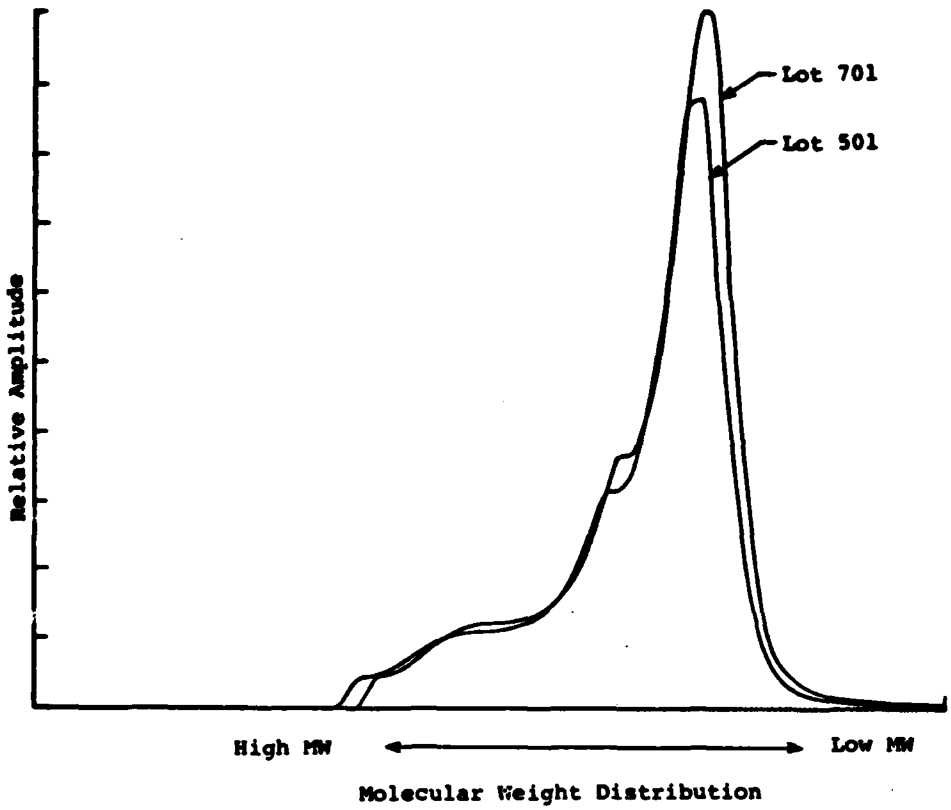


Figure 5. Molecular Weight Distribution Differences Between Lots of Allied 15V

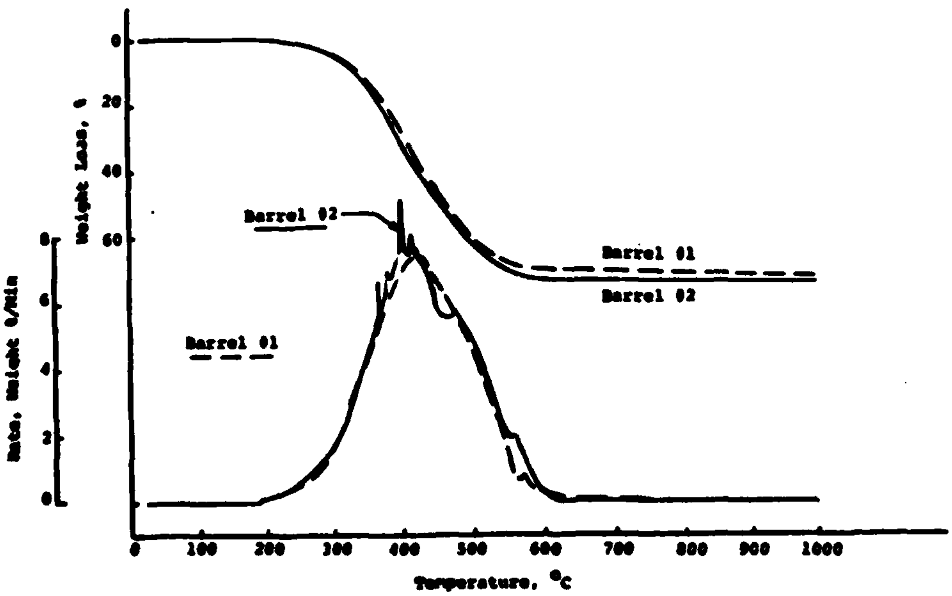


Figure 6. TGA of Two Barrels of Allied 15V - Lot 501

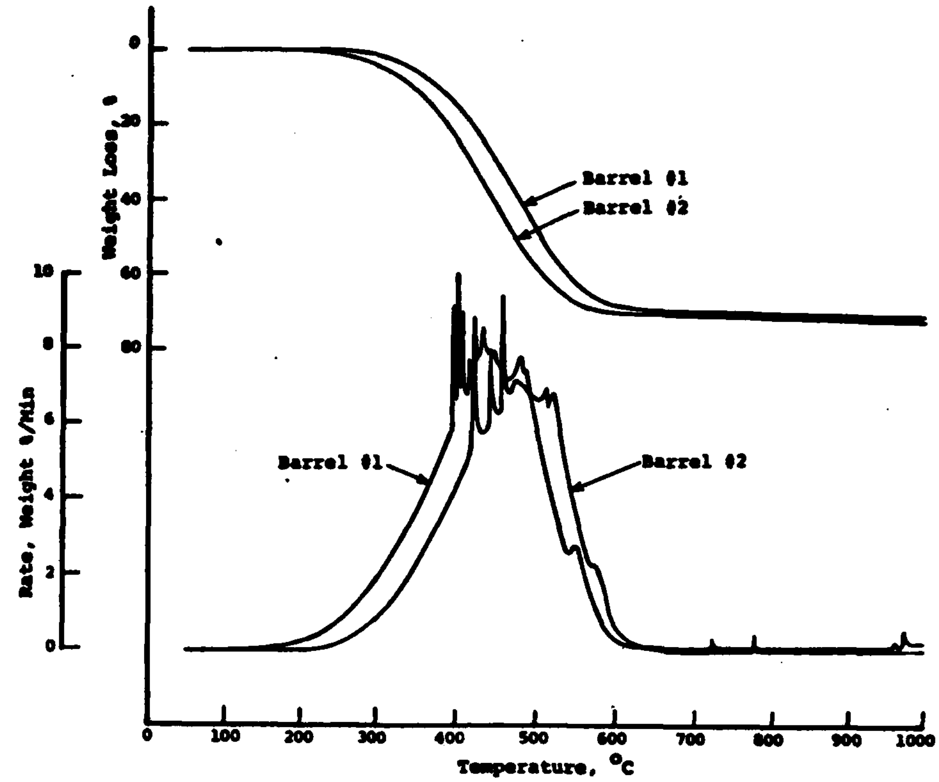


Figure 7. TGA of Two Barrels of Allied 15V - Lot 701

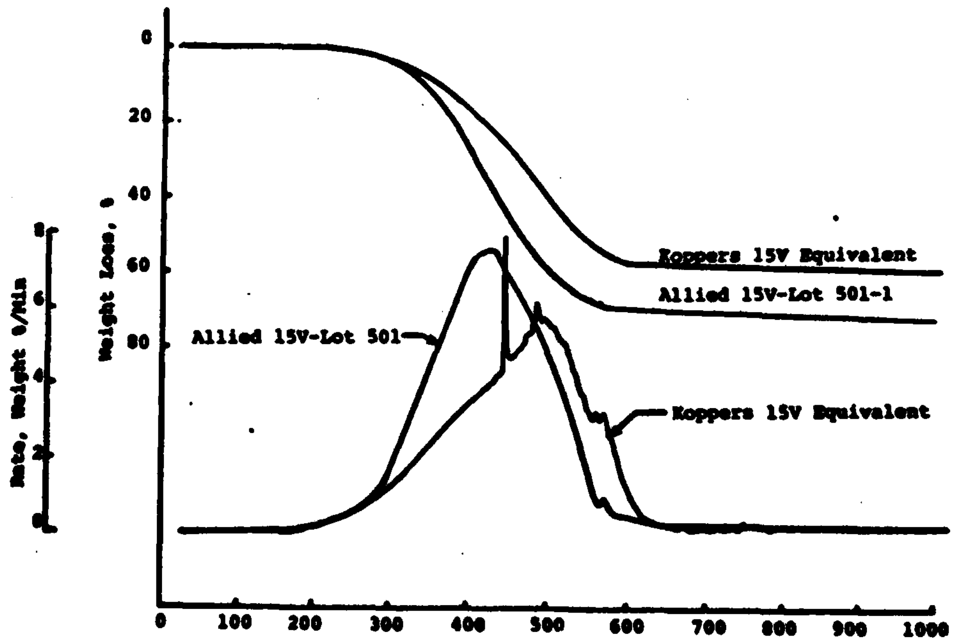


Figure 8. TGA Differences Between Koppers and Allied 15V

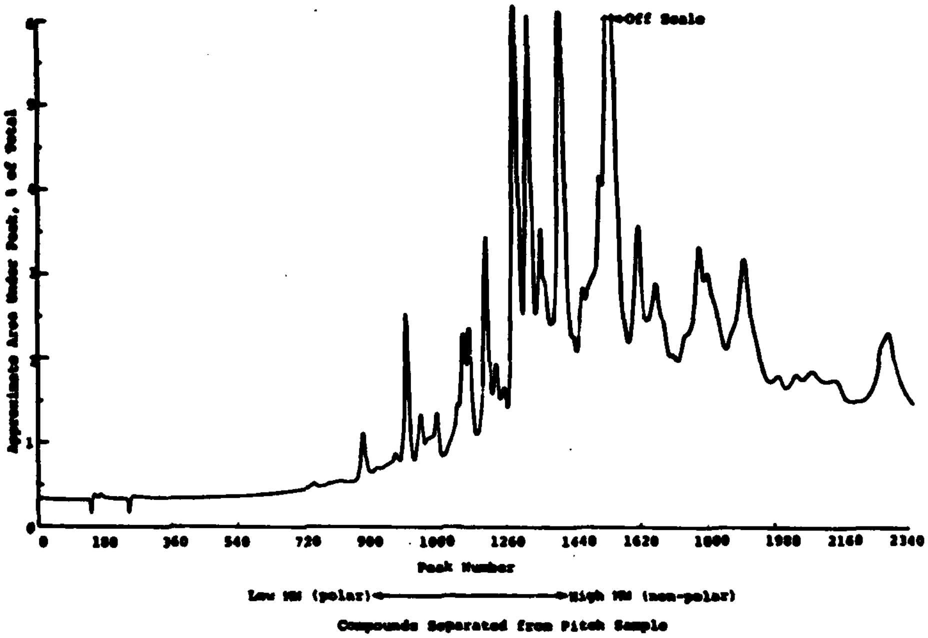


Figure 9. High Pressure Liquid Chromatogram of Allied 15V - Lot 701 Coal Tar Pitch

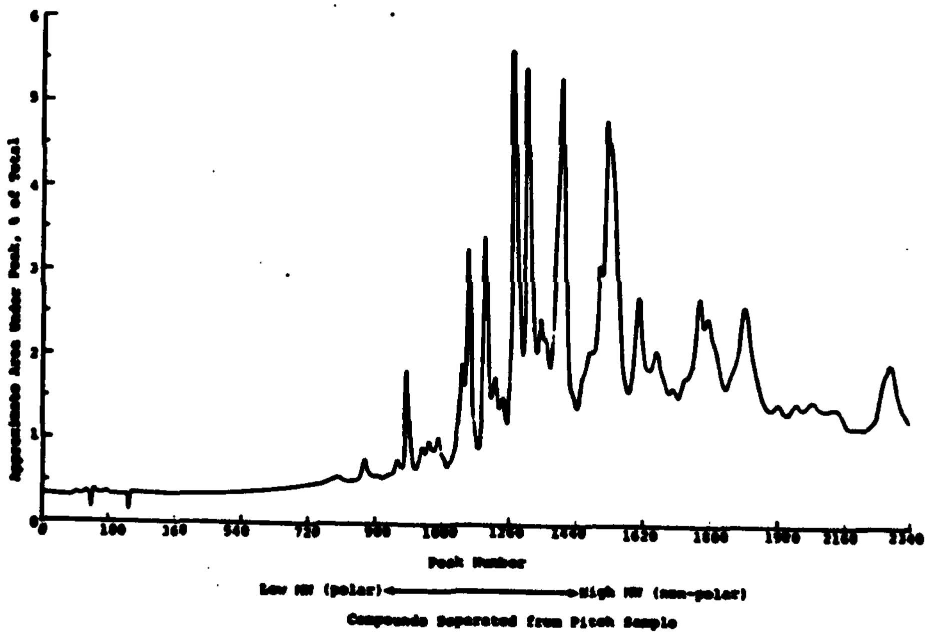


Figure 10. High Pressure Liquid Chromatogram of Koppers 15V Equivalent Coal Tar Pitch

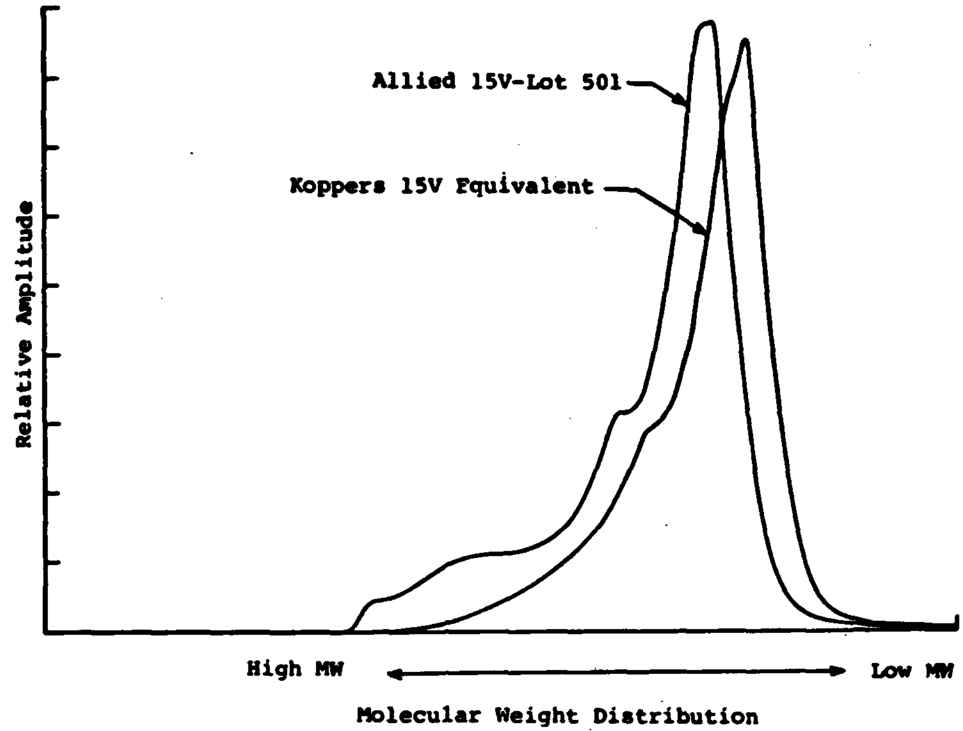


Figure 11. Compositional Differences Between the Allied and Koppers Version of 15V Pitch

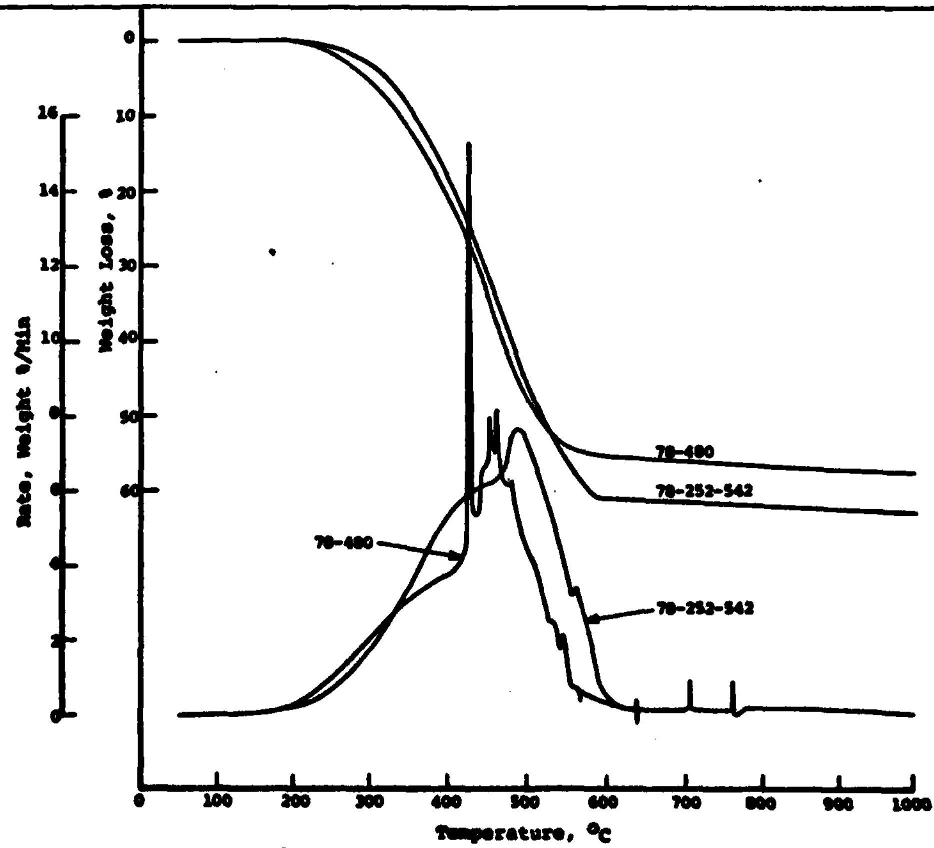


Figure 12. TGA of Koppers Experimental Pitches

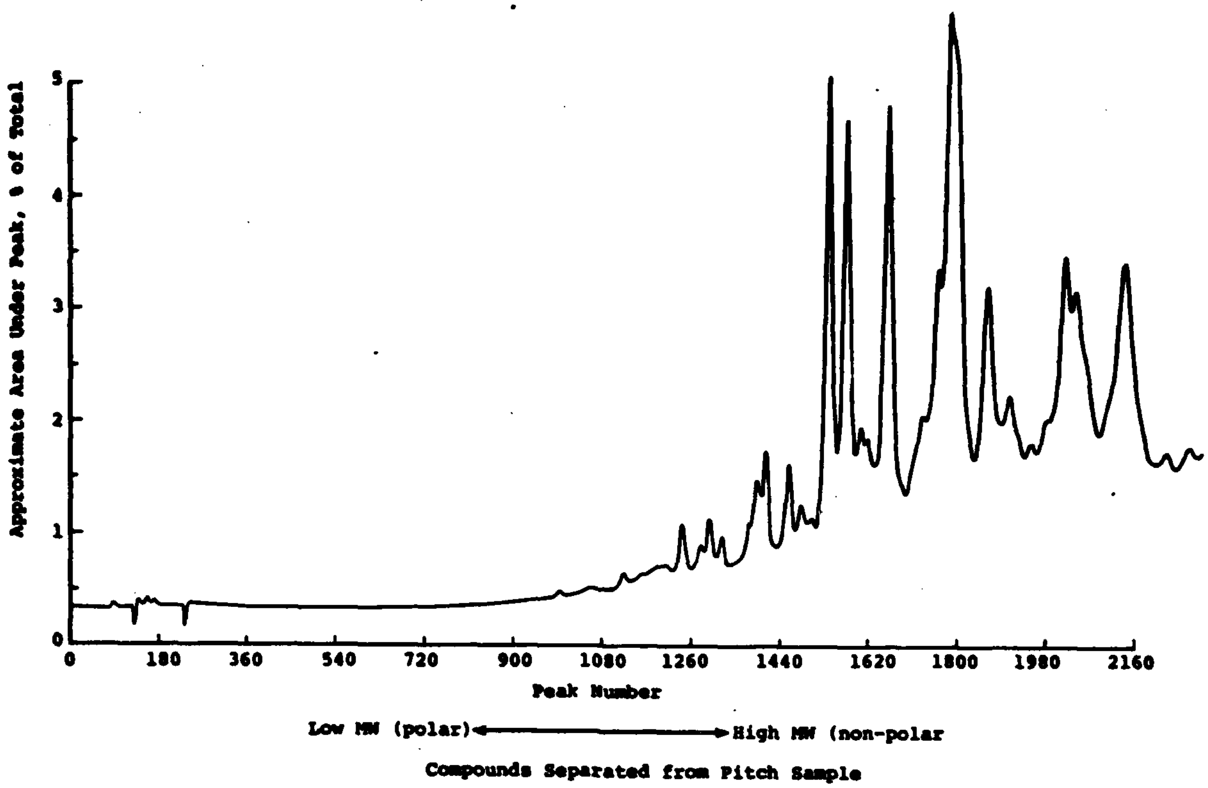


Figure 13. High Pressure Liquid Chromatogram of Koppers Experimental Impregnating Pitch #78-252-480

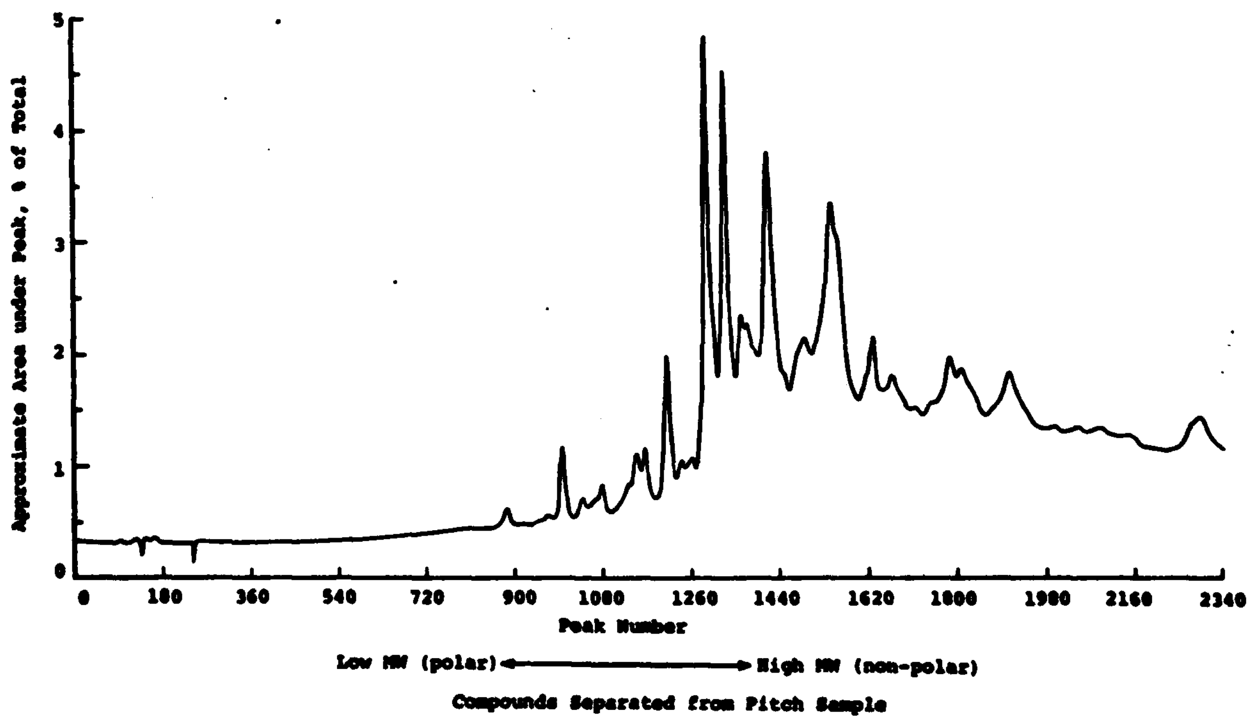


Figure 14. High Pressure Liquid Chromatogram of Koppers Experimental Impregnating Pitch #78-480

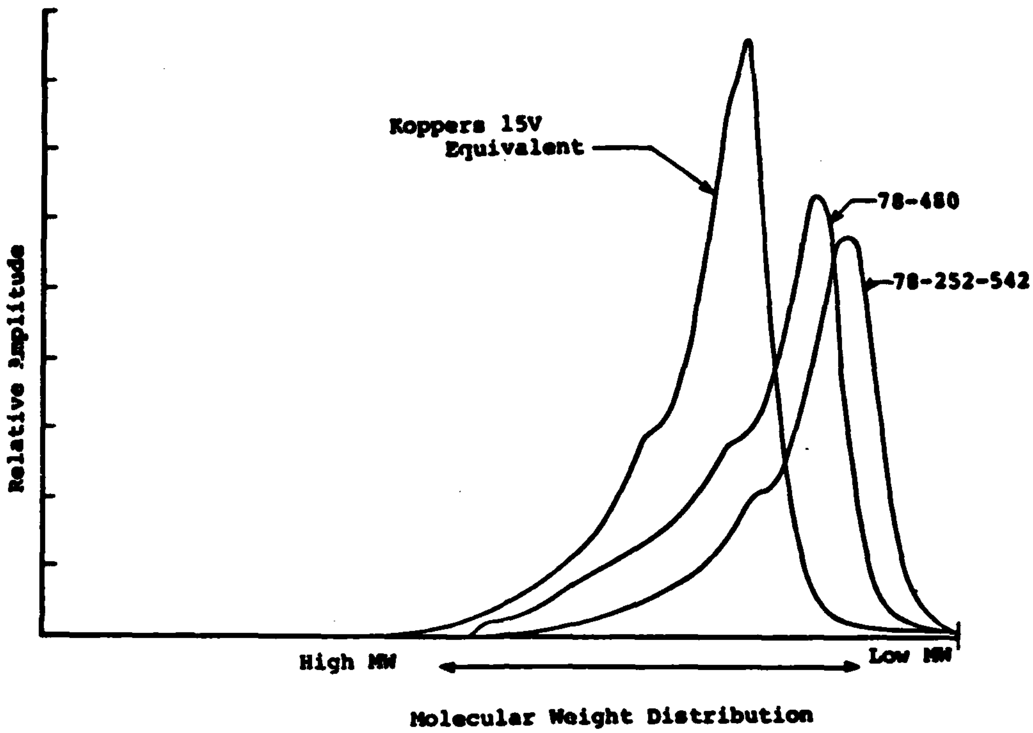


Figure 15. Compositional Differences of Three Koppers Pitches

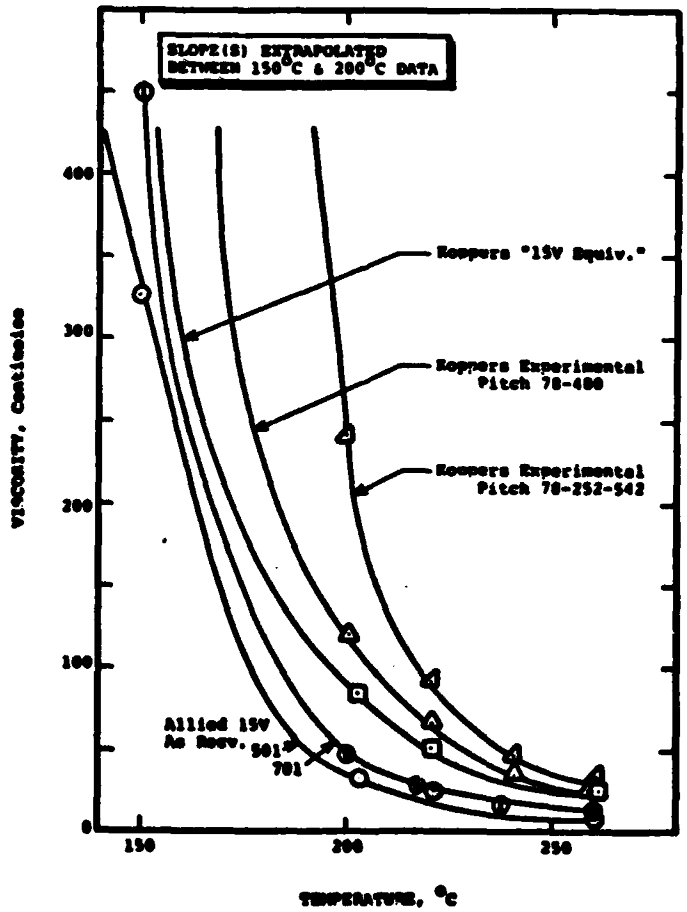


Figure 16. Viscosities of 15V Pitches and Two Experimental Koppers Pitches

same time, Lot 701 appears to be less uniform as shown in typical TGA data in Figures 6 and 7 whereas the data obtained for Lot 501 was much more reproducible than Lot 701.

TGA data, high pressure liquid chromatography measurements, and gel permeation data are presented in Figures 8, 9, 10 and 11 to contrast the composition and basic decomposition of Koppers 15V Equivalent pitch material with Allied 15V. Figures 12, 13, 14 and 15 present the same type of signature for two Koppers experimental pitches designated (by Koppers) as 78-252-480, and 78-480. The viscosity of these pitches are compared in Figure 16 with viscosities measured for Allied 15V, Lot 501 and Lot 701, and Koppers 15V Equivalent.

4. Heat Treatment of Coal Tar Pitch

The effect of heat treating to improve the char yield of as received Allied 15V pitch was thoroughly investigated. The dependance upon the temperature, residence time and the effect of mechanically agitating (mixing) the liquid mass of pitch undergoing conditioning were parametrically analyzed. Table 4 shows the quinoline insoluble content of several conditions of pitch (as received and pre-treated).

Because the treating of pitch to increase the carbon yield upon impregnation and carbonization is an ancillary task undertaken to understand basic composition characteristics, the data has been placed in Appendix 1 (TGA and viscosity) and Appendix 2 (Mesophase Formation).

Table 4

QUINOLINE INSOLUBLE CONTENT OF TREATED PITCH

| IMPREGNATING PITCH | CONDITION | QUINOLINE INSOLUBLES, % |
|---|---|---|
| Allied 15V | As Recv. - Lot 501, Bbl #1 | 2.2 |
| Allied 15V | As Recv. - Lot 501, 861 #7 | 3.0 |
| Koppers "15V Equiv." | As Recv. - 1977 Distilled | 7.1 |
| Allied 15V | HT @ 405°C-14 hrs-w/o Agitation | 6.3 |
| Allied 15V | GT @ 405°C-14 hrs-with Agitation | 8.8 |
| Allied 15V | HT @ 405°C-20 hrs-w/o Agitation | 10.8 |

5. Decomposition Reactions

Experimental packages with and without fiber modifications have been conducted according to the Air Force's EISP schedule to provide material for chemical and physical measurements and analysis. Carbonization runs at 3, 5, 10 and 15 ksi have been carried out to the completion of the EISP schedule. They have been interrupted (Figure 17) and rapidly quenched to freeze in properties and the composition of liquid pitch prior to transformation of the pitch to a solid state. Figures 18, 19, 20, 21 and 22 compare the properties and compositional characteristics of as received Allied 15V and partially carbonized (at 15 ksi) Allied 15V recovered by the hot recovery technique developed specifically for retrieving liquid pitch samples. Figure 23 compares the distribution of the molecular weights of recovered liquid pitch from a 15 ksi run with the molecular weight signature of Koppers 15V Equivalent. Figures 24 and 25 present the high pressure liquid chromatogram from fully completed EISP carbonization schedules at 10 ksi and 15 ksi, respectively.

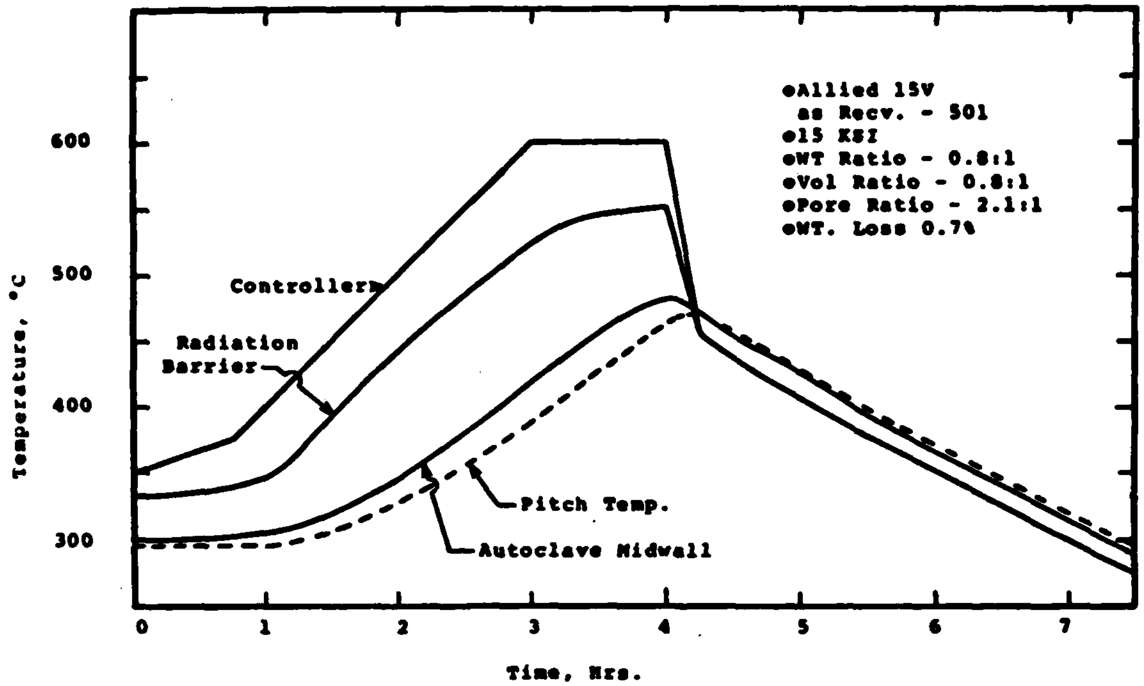


Figure 17. Time-Temperature-Pressure History of Interrupted 15 KSI Carbonization (EISP Schedule)

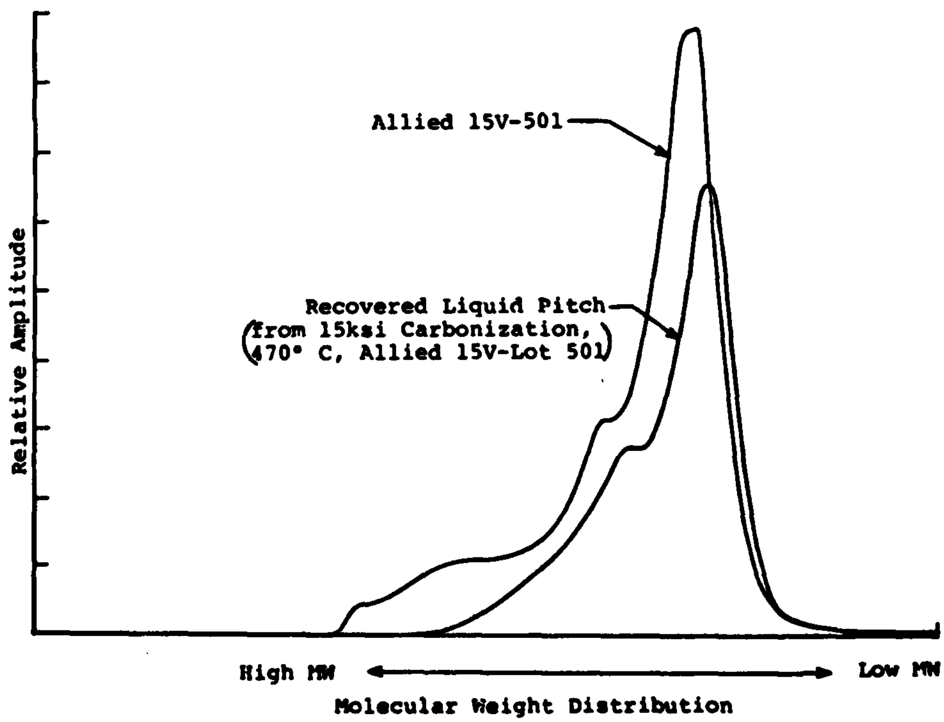


Figure 18. Gel Permeation Data Showing Shift in Molecular Weight Distribution Due To Partial Carbonization of 15 KSI

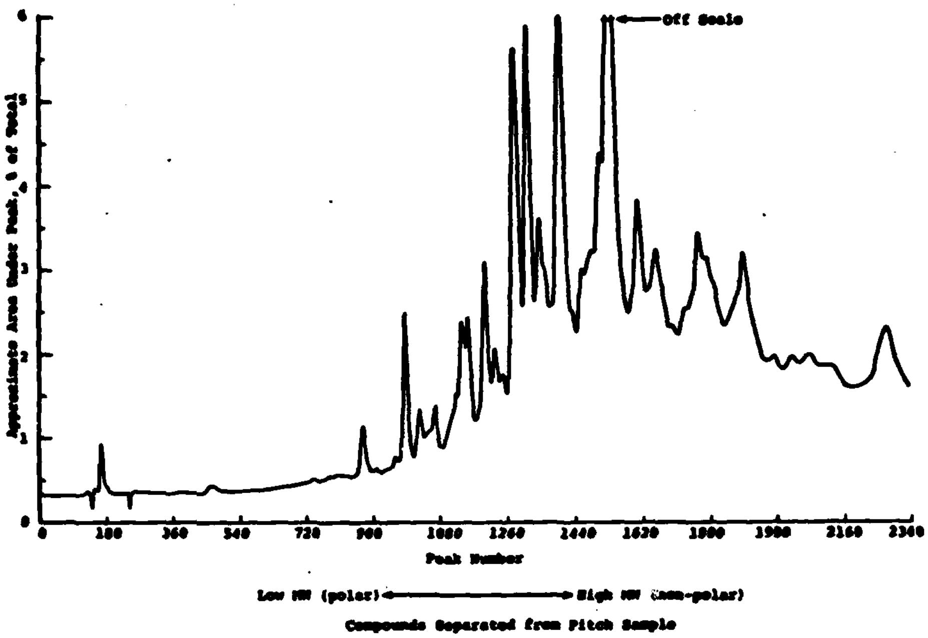


Figure 19. High Pressure Liquid Chromatogram of Allied 15V - Lot 501 Coal Tar Pitch Precursor

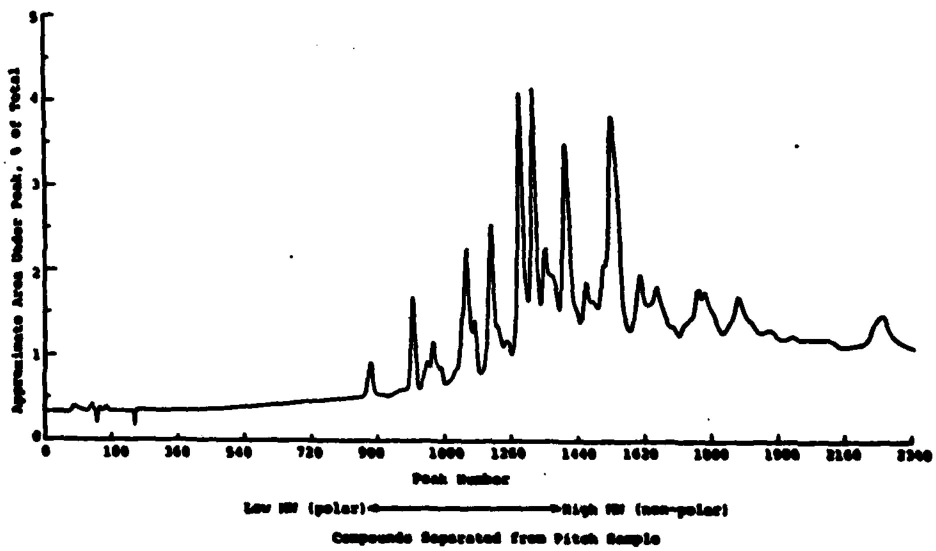


Figure 20. High Pressure Liquid Chromatogram of Hot Recovered Liquid Pitch (Allied 15V - Lot 501) from Interrupted (470°C) 15 KSI Carbonization

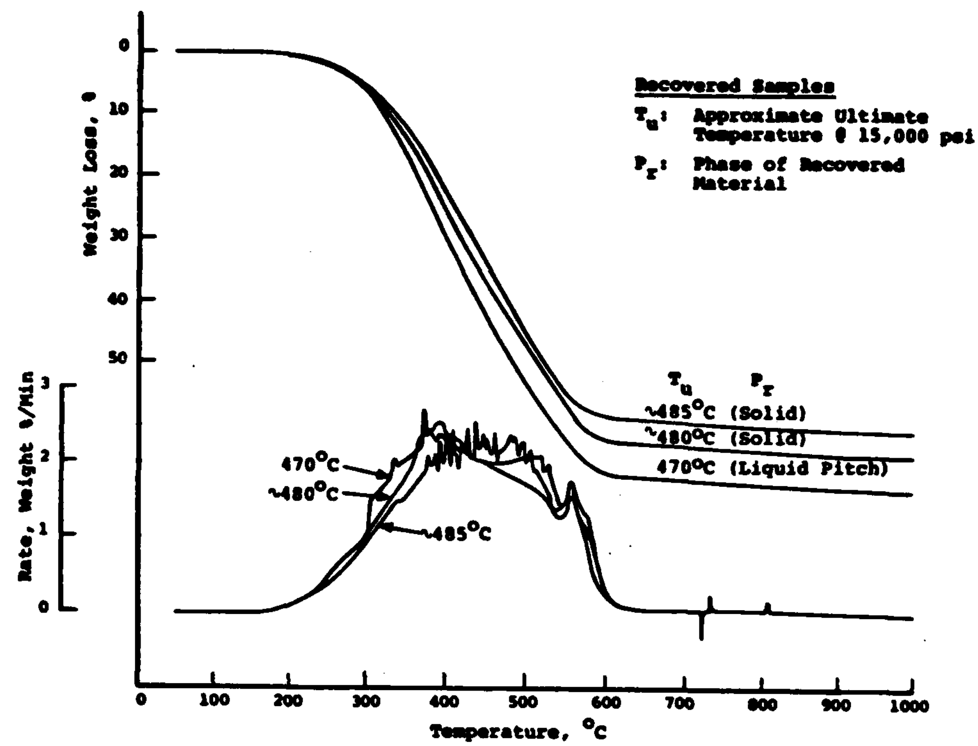


Figure 21. Weight Loss Comparison Between Liquid Pitch and Solid Pitch Recovered Hot from Interrupted 15 KSI Carbonization Cycle (TGA Data)

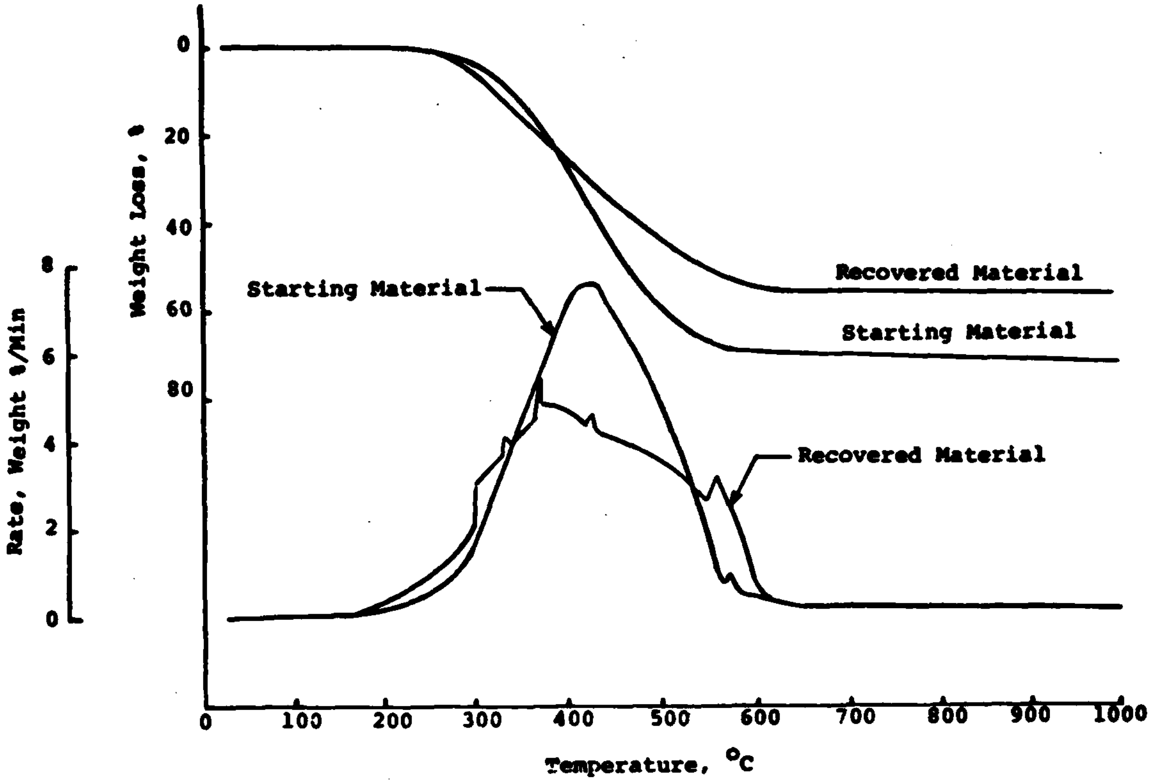


Figure 22. TGA Data Comparing Weight Loss Characteristics of Recovered Liquid Pitch from Interrupted Run with Starting Material

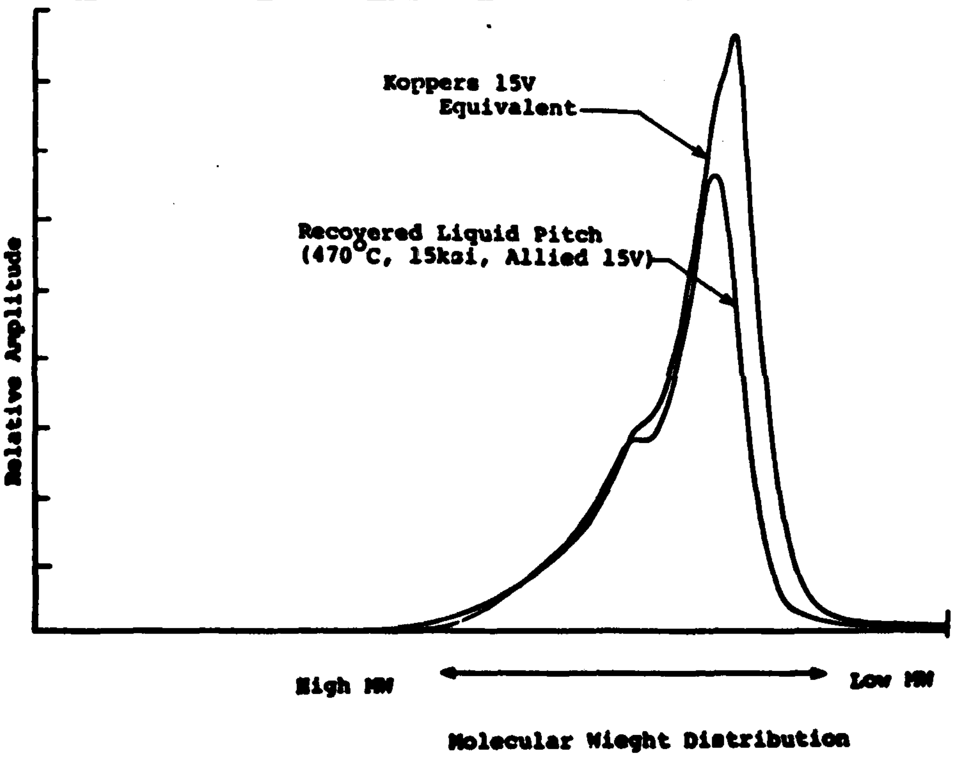


Figure 23. Gel Permeation Data Showing Compositional Similarity Between Partially Carbonized Allied 15V and Koppers 15V Equivalent (As Received)

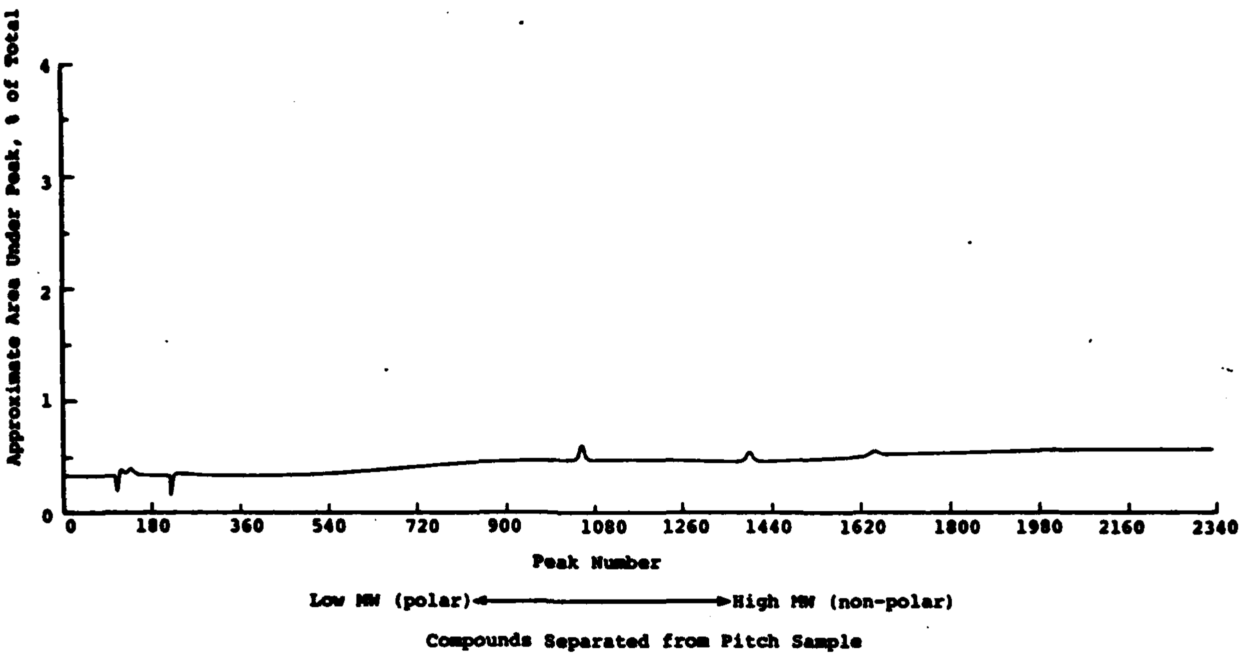


Figure 24. High Pressure Liquid Chromatogram of Allied 15V Carbonized to Completion via EISP Schedule at 10 KSI

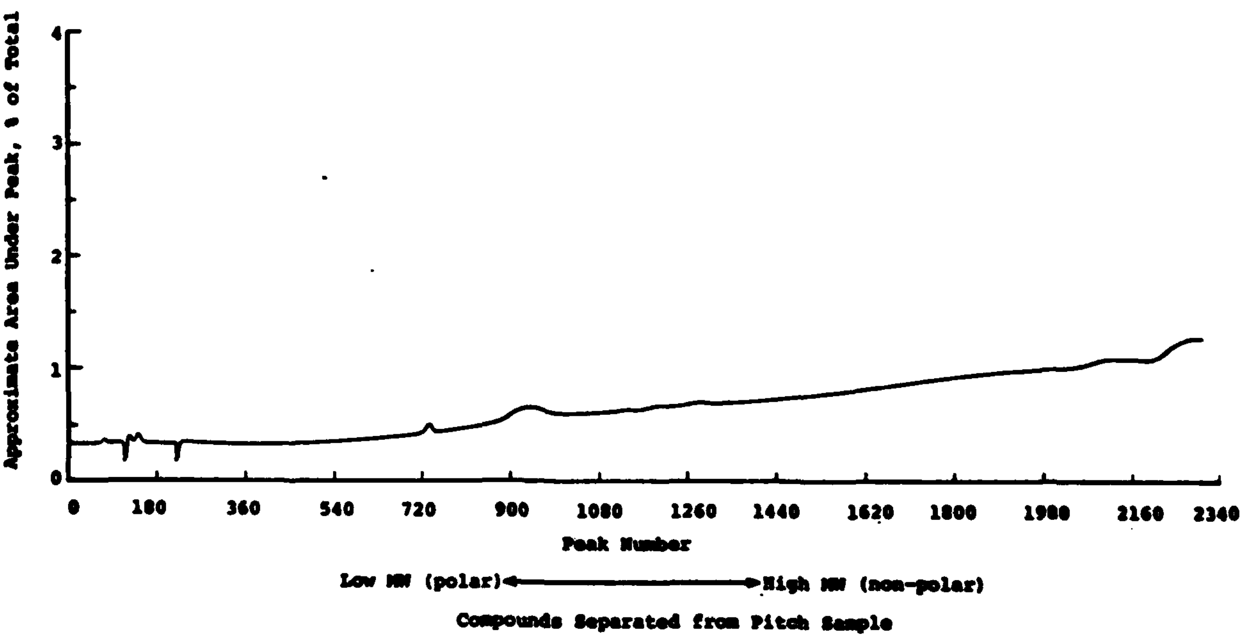


Figure 25. High Pressure Liquid Chromatogram of Allied 15V Carbonized to Completion via EISP Schedule at 15 KSI

The elemental analysis of Allied 15V pitch material as a function of the degree of processing is presented in Tables 5 and 6. The properties of carbonized pitch for several process conditions and degree of completeness is presented in Table 7. It is important to note in Table 7 that while the bulk density of pitch carbonized to 470°C and then rapidly quenched (Run No. 005/SE) is similar to bulk properties of the material processed at higher temperatures, the true density (apparent) and porosity of the recovered material is significantly different. These differences can be accounted for if it is assumed that the material recovered had not completed, or was in the initial stages of transformation from a liquid to a solid.

A summary of the results of thermogravimetric analysis of partially carbonized coal tar pitch is shown in Table 8. The specimens were prepared at 5 and 15 ksi and several different carbonization temperatures. The significant fact that can be derived from the table is the temperature at which maximum weight loss occurs is a function of the highest previous temperature to which the specimen had been heated. This is amplified in Figure 26 which shows the weight loss dependence on carbonization temperature and residence time at that temperature. The conclusion that can be drawn from Figure 26 is that the longer time at temperature, the greater the weight loss with temperature ramping resulting in the least weight loss.

The effect of carbonization pressure on coal tar pitch density and porosity is shown in Figure 27. As one would expect with increasing pressure the porosity decreases and the density increases. It was also discovered that in this autoclave that the vertical location in the sealed can also had an influence on the carbonized pitch properties. This effect on

Table 5

ELEMENTAL ANALYSIS OF ALLIED 15V-LOT 501
AS FUNCTION OF DEGREE OF CARBONIZATION AT 15,000 PSI

| | COMPOSITION BY WEIGHT PERCENT | | | | | |
|---|---|---|---|---|---|---|
| MATERIAL CONDITION | C | H | N | S | O | Ash |
| As Received | 92.42 | 4.83 | 1.07 | 0.55 | 1.03 | 0.15 |
| Carbonized to 470°C | 92.33 | 4.54 | 0.96 | 0.40 | 1.49 | 0.29 |
| Full Carbonization | 93.07 | 2.72 | 0.92 | 0.50 | 2.69 | 0.10 |

Table 6

ELEMENTAL ANALYSIS OF ALLIED 15V-Lot 501

AS FUNCTION OF PRESSURE FOR FULL CARBONIZATION* RUNS

| | COMPOSITION BY WEIGHT PERCENT | | | | | |
|---|---|---|---|---|---|---|
| CARBONIZATION PRESSURE | C | H | N | S | O | Ash |
| 10,000 psi | 92.43 | 2.36 | 0.83 | 0.44 | 3.93 | 0.34 |
| 15,000 psi | 93.07 | 2.72 | 0.92 | 0.50 | 2.69 | 0.10 |

* Identical carbonization cycles with exception of pressure - EISP schedule to 615°C pitch temperature, then held 5 hours.

Table 7

PROPERTIES OF CARBONIZED PITCH
FOR SEVERAL PROCESS CONDITIONS

| RUN NO. | PRESSURE KSI | MAX PITCH TEMP., °C | RESIDENCE TIME HRS. | AUTOCLAVE LOCATION | BULK* DENSITY gm/cc | APPARENT* DENSITY gm/cc | POROSITY % |
|---|---|---|---|---|---|---|---|
| CARBONIZED ALLIED 15V | | | | | | | |
| 002/SE | 10 | 615° | 1 | Top | 1.15 | 1.47 | 21.8 |
| | | | | Bottom | 1.09 | 1.51 | 27.8 |
| 003/SE | 10 | 615° | 4 | Top | 1.13 | 1.52 | 25.7 |
| | | | | Bottom | 1.00 | 1.59 | 37.1 |
| 004/SE | 15 | 605° | 4 | Top | 1.20 | 1.62 | 25.9 |
| | | | | Bottom | 1.06 | 1.63 | 35.0 |
| 005/SE | 15 | 470° | <0.25 | Top | 1.10 | 1.25 | 12.0 |
| IMPREGNATED POROUS CARBON | | | | | | | |
| 003/SE | 10 | 615° | 4 | Middle | 1.46 | 1.85 | 21.0 |
| | | | | Bottom | 1.48 | 1.94 | 23.7 |
| 004/SE | 15 | 605° | 4 | Top | 1.51 | 1.85 | 18.4 |
| | | | | Middle | 1.52 | 1.86 | 18.3 |
| | | | | Bottom | 1.52 | 1.86 | 18.3 |
| 005/SE | 15 | 470° | <0.25 | Top | 1.44 | 1.62 | 11.1 |
| | | | | Middle | 1.52 | 1.69 | 10.1 |
| | | | | Bottom | 1.51 | 1.67 | 9.6 |

*ASTM C-20

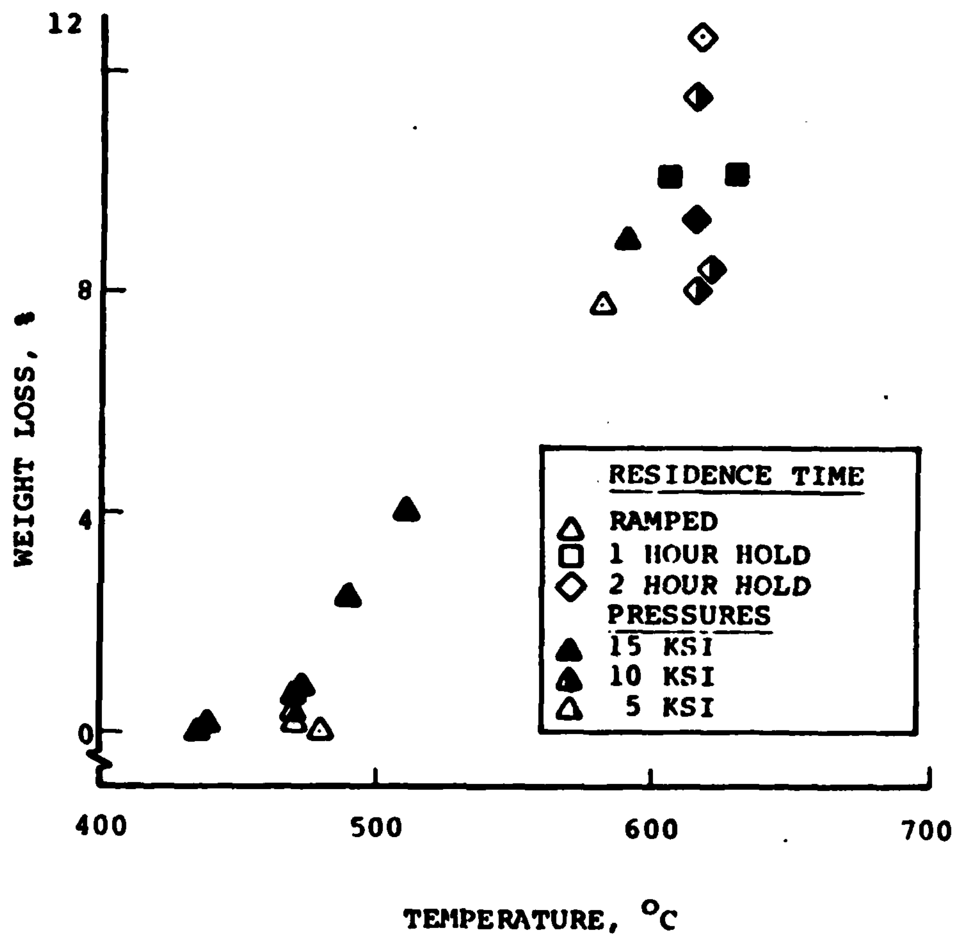


Figure 26. WEIGHT LOSS DEPENDENCE ON ULTIMATE CARB TEMPERATURE AND TIME

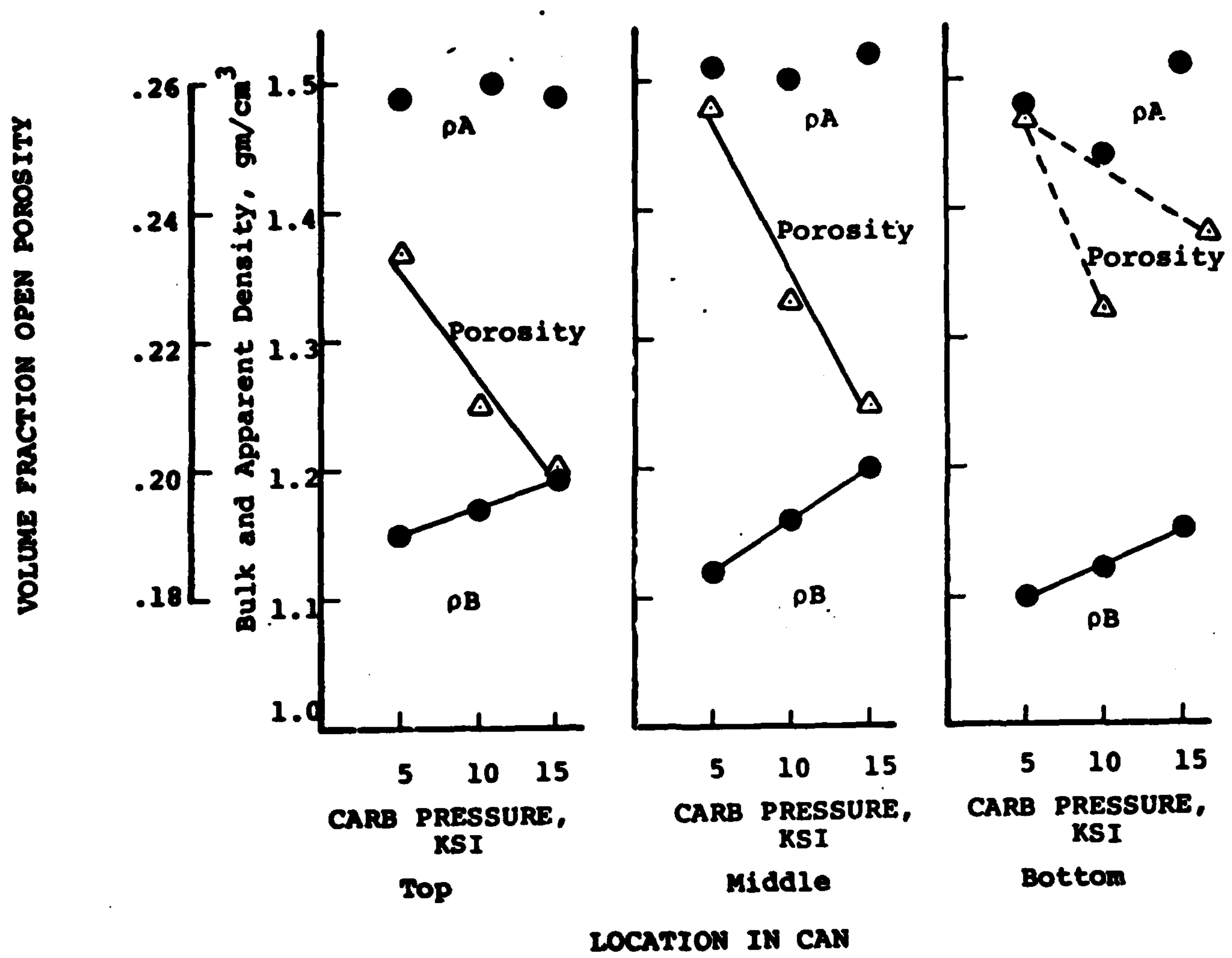


Figure 27. PRESSURE DEPENDENCE OF CARBONIZED 15V COAL TAR PITCH PROPERTIES FOR 620°C CARB TEMPERATURE HELD 2 HOURS

the bulk and apparent density of the carbonized pitch also was apparent when the material was carbonized at a lower temperature as shown in Figure 28.

Table 8

THERMOGRAVIMETRIC ANALYSIS OF PARTIALLY CARBONIZED 15V COAL TAR PITCH

| Carb Pressure, ksi | Previous Temperature, (°C) | Char Yield @ 1000°C (%) | Max Rate Temp. (°C) | Loss Rate (Mg/Min) |
|---|---|---|---|---|
| 15 | 620 | 97.8 | 900 | <0.10 |
| 15 | 510 | 88.7 | 430 | 0.38 |
| 15 | 470 | 43.8 | 370 | 2.10 |
| 5 | 620 | 96.7 | 800 | 0.12 |
| 5 | 582 | 91.9 | 450 | 0.15 |
| 5 | 480 | 43.5 | 390 | 2.10 |

6. Mechanical Properties of Carbonization Coal Tar Pitch

Three point flexural bending tests were done on the partially and fully carbonized coal tar pitch material. Evaluation of the date showed that there was a significant effect of specimen location in the can on the material properties. The variation of ultimate flexural bending stress with location in the can is shown in Figure 29. The significant fact that can be drawn from this figure is that there is a variation in the ultimate stress of a factor of approximately 3 between the specimens taken from the bottom of the can and those taken from the top. This same trend is shown in Figure 30 which had a higher operating pressure and ultimate temperature. The same trend toward higher properties from material at the top of the can is shown in Figures 31 and 32 which show the elastic modulus of the specimens processed at 5 ksi

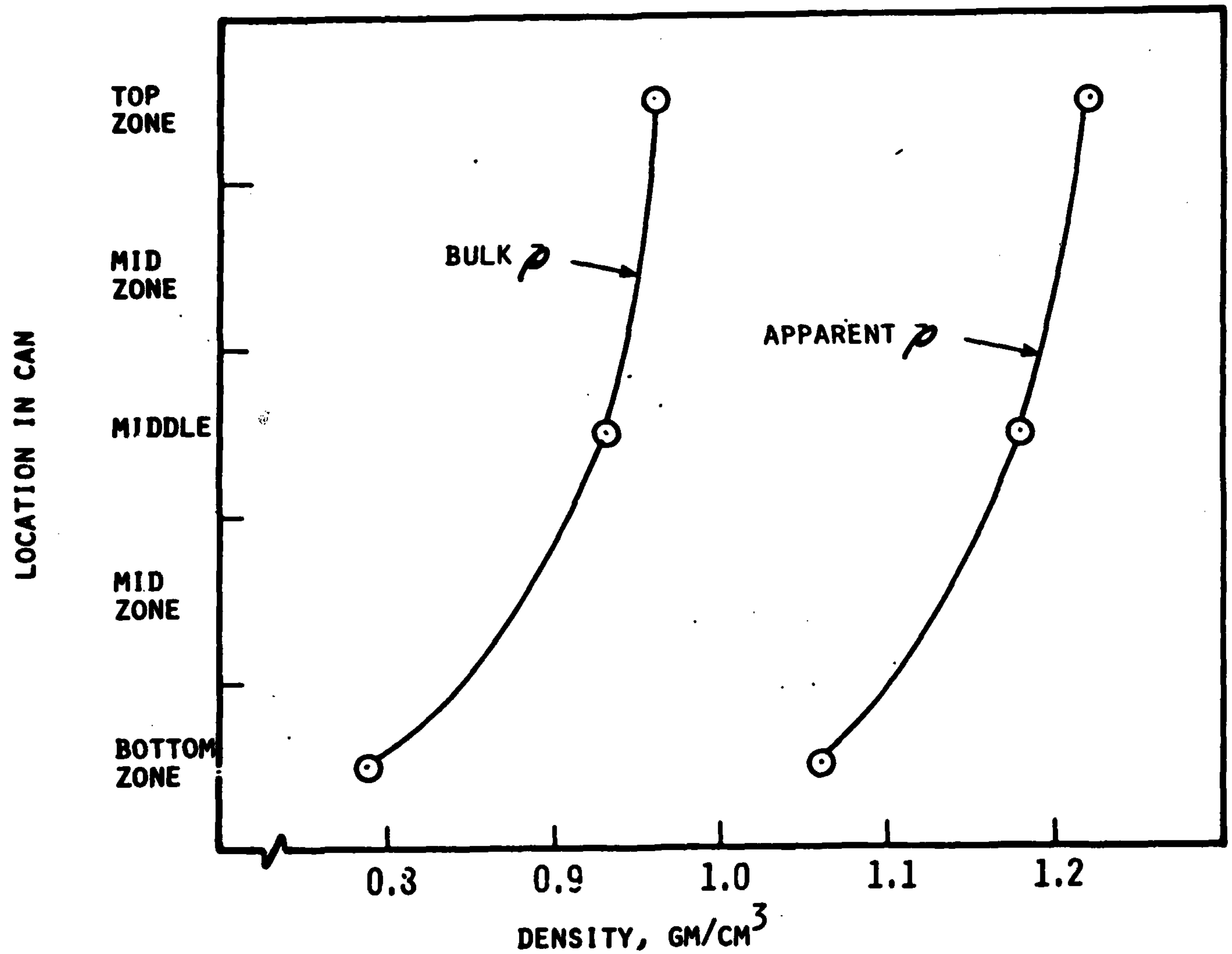


Figure 28. DENSITY OF 15V PITCH CARBONIZED TO 470°C AT 15 KSI

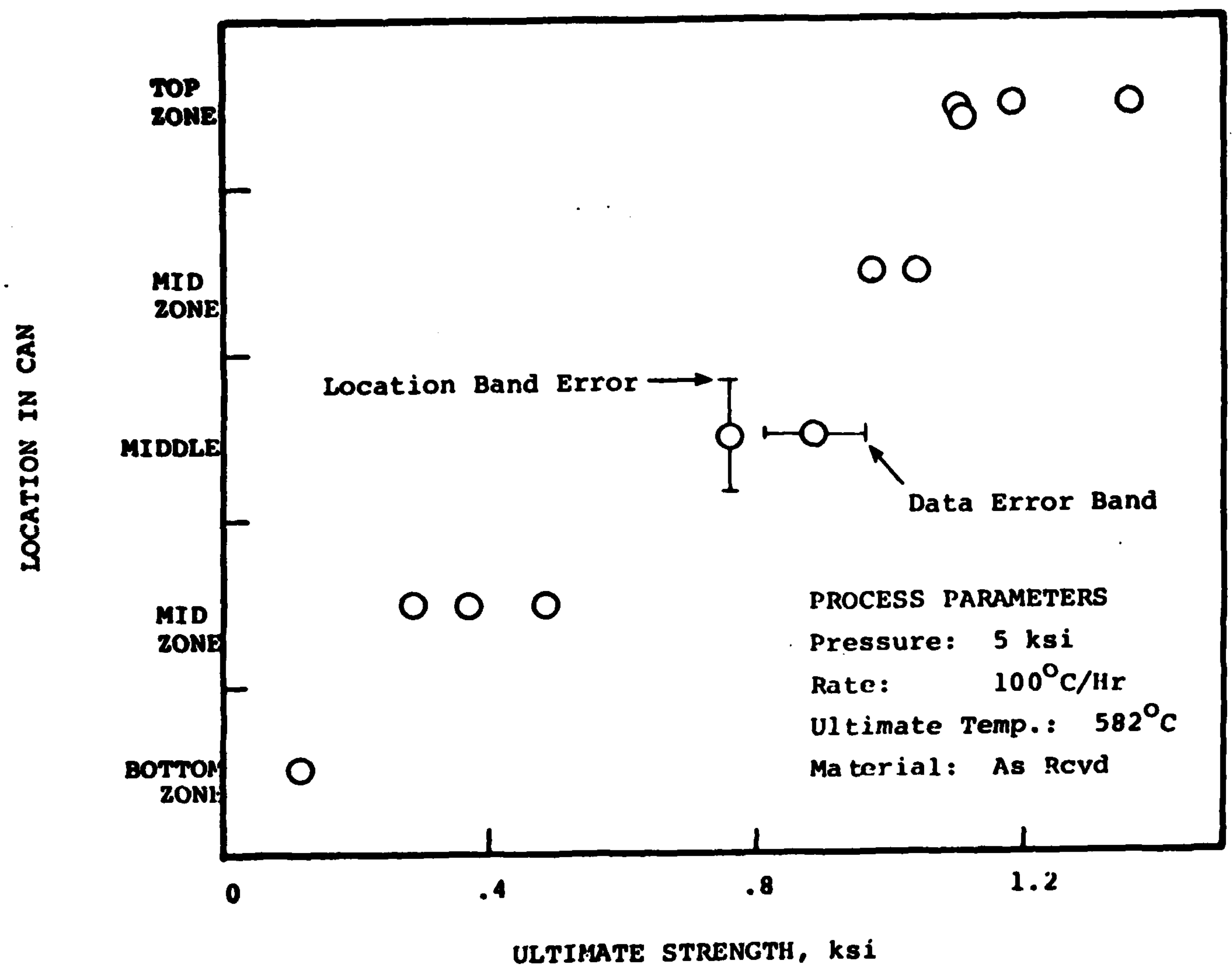


Figure 29. EFFECT OF CAN LOCATION UPON THE FLEXURAL STRENGTH OF PARTIALLY CARBONIZED 15V COAL TAR PITCH AT 5 KSI

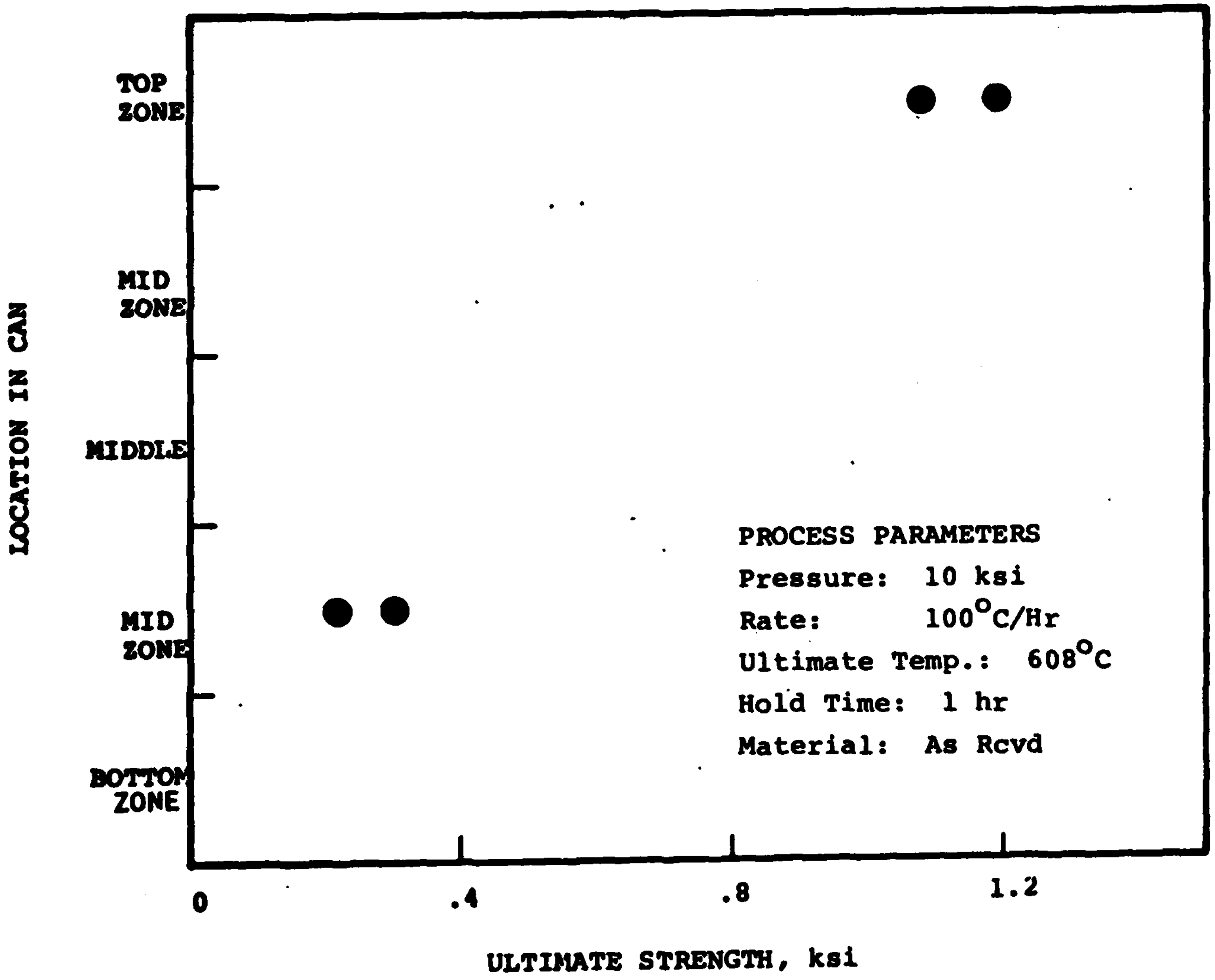


Figure 30. EFFECT OF CAN LOCATION UPON THE FLEXURAL STRENGTH OF CARBONIZED 15V COAL TAR PITCH - 10 KSI

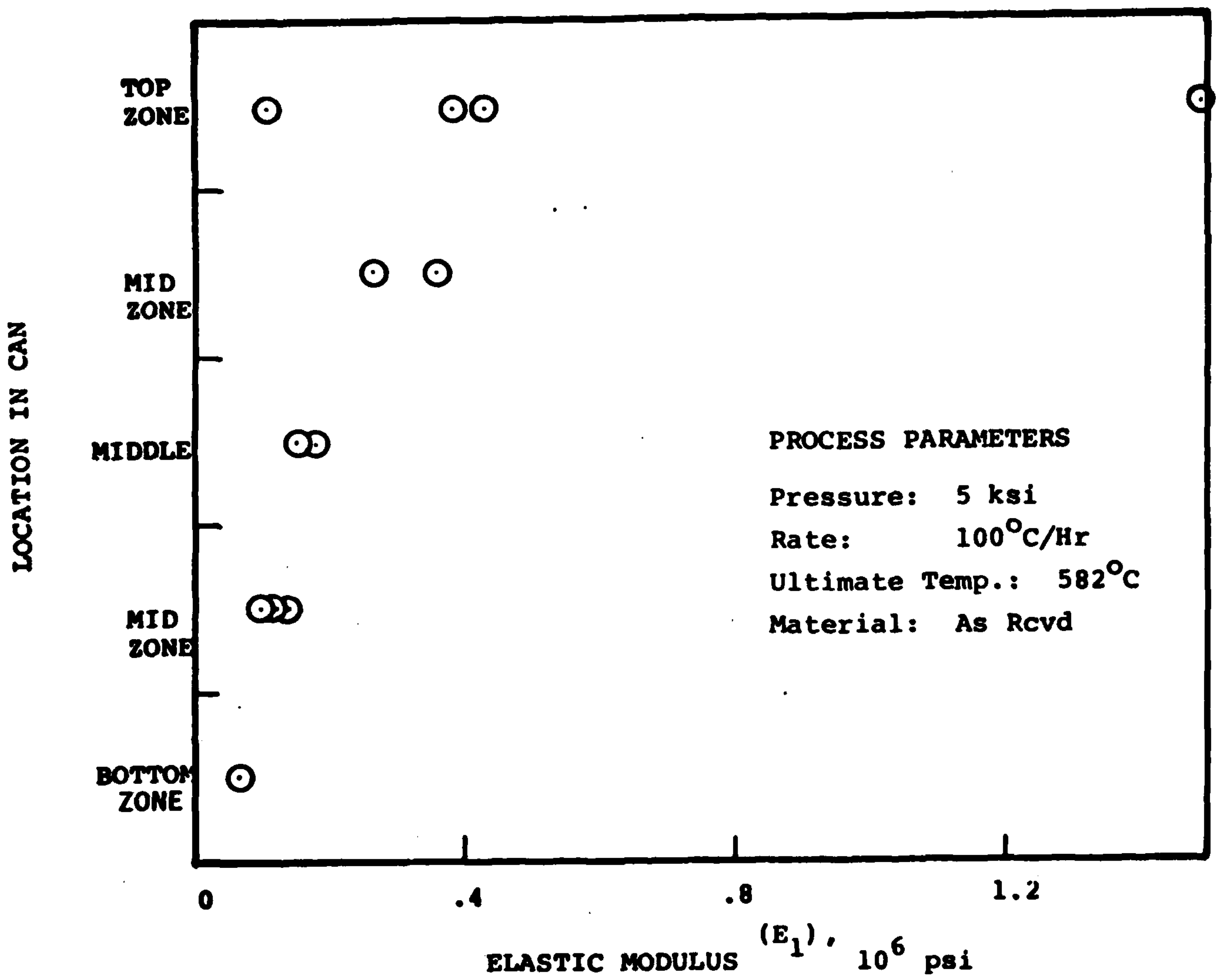


Figure 31. EFFECT OF CAN LOCATION UPON THE INITIAL ELASTIC MODULUS, $E_1$, OF PARTIALLY CARBONIZED COAL TAR PITCH

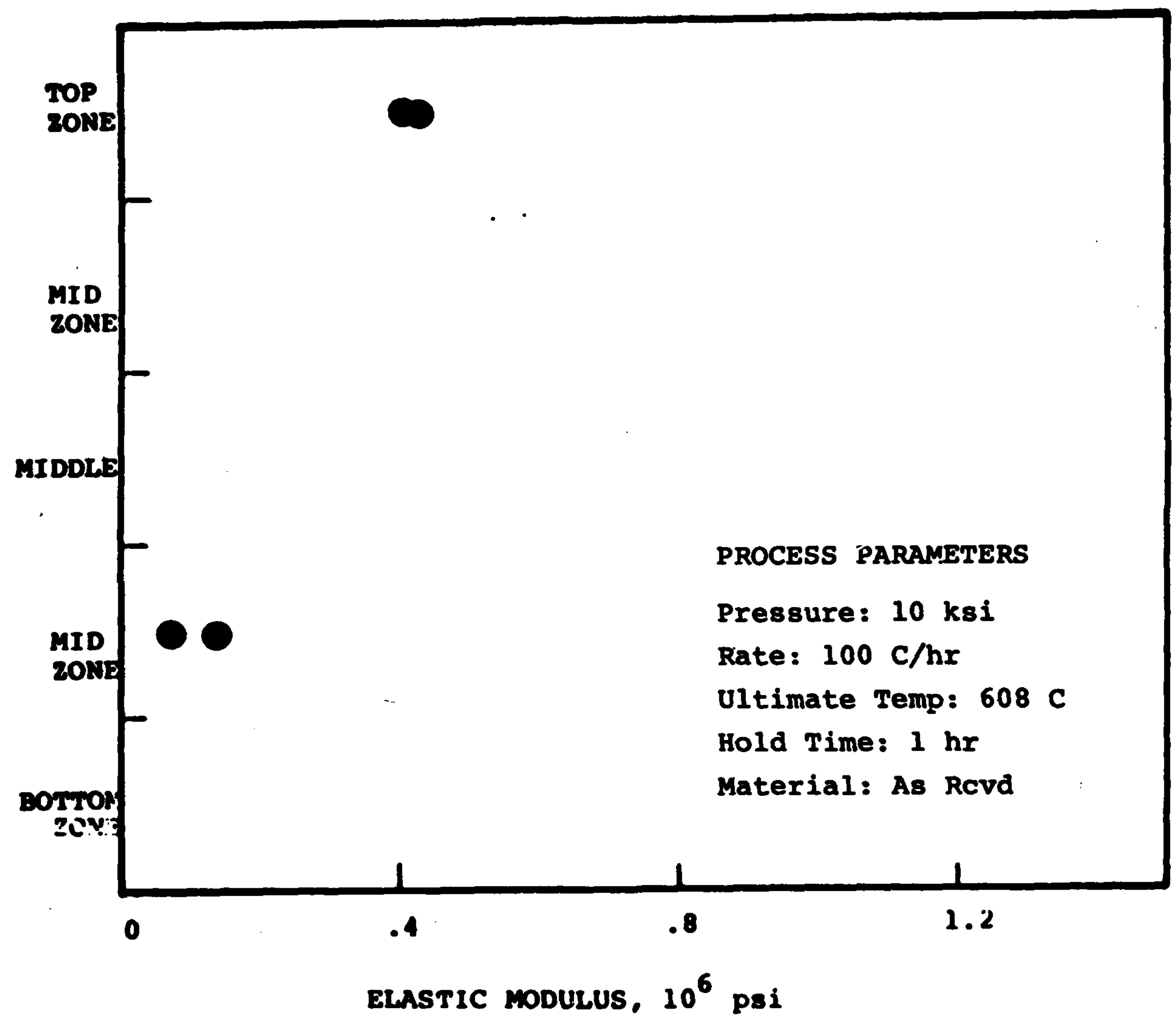


Figure 32. MODULUS OF 15V COAL TAR PITCH CARBONIZED AT 10 KSI

(582°C maximum temperature) and 10ksi (608°C maximum temperature) respectively. All of the ultimate flexural stress and strain data is plotted together in Figure 33.

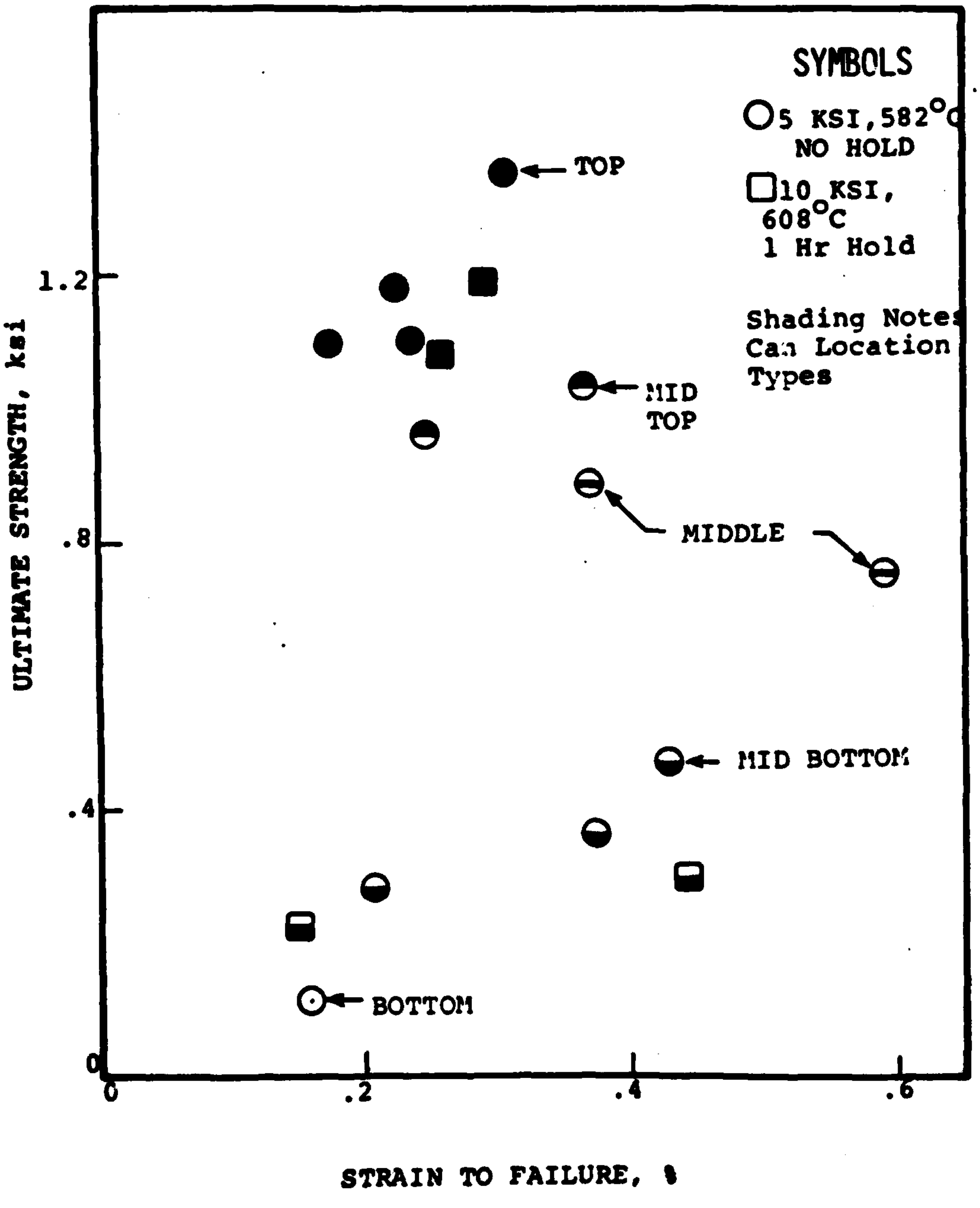


Figure 33. CAN LOCATION INFLUENCE UPON PROPERTIES OF CARBONIZABLE COAL TAR PITCH

# V. CONCLUSIONS

Based on the results of the study, conclusions can be drawn in the areas of; coal tar pitch characterization, heat treatment of pitch, decomposition reactions of pitch and mechanical properties of pitch. The conclusions are as follows:

1) Characterization specifications for coal tar pitches used in the Air Force Equivalent Industrial Standard Process (EISP) should be rewritten to take into account the change in the characteristics of coal tar pitch material over long periods of time and also the increase in softening point in the thermally pretreated pitches.

2) Thermal pretreatment of pitch combined with mechanical agitation of the pitch can result in the following:

   a. More reproducible batches for impregnation.
   b. Increase in char yield.
   c. Increase in temperature range where the decomposition occurs and reduction of gas evolution during liquid state.
   d. Reduction in average molecular weight by reducing long chain polymers.
   e. Reduction in maximum rate of decomposition.

3) From studies of the decomposition of coal tar pitch, the following conclusions can be drawn:

   a. The apparent and bulk density of coal tar pitch at the liquidus-solidus transition temperatures is on the order of 1.10 to 1.25 $gm/cm^3$.

b. Stratification of variant properties and microstructure of carbonized coal tar pitch occurs in sealed cans at all pressures.

c. The weight loss of decomposing coal tar pitch in sealed cans appears to be independent of pressure and a linear function of ultimate temperature during carbonization

d. Evaluation of coal tar pitch carbonized at 5 ksi and 15 ksi indicate that the complete carbonization occurs at temperatures greater than 620°C. The 15 ksi process is slightly more efficient in terms of char yield at 620°C but probably is not as efficient at lower temperatures

4. The elastic modulus and ultimate strength from flexure tests of carbonized pitch is on the order of $.4 \times 10^6$ psi and 1200 psi, respectively. Partially carbonized pitch (to 470°C at 15 ksi) appears to have similar properties.

# A P P E N D I X 1

## THERMOGRAVEMETRIC ANALYSIS (TGA) AND VISCOSITY DATA FOR HEAT TREATED COAL TAR PITCHES

(Figures)

| MATRIX/CONDITION | TEMP. °C | MAX RATE % PER MIN |
|---|---|---|
| ● AS RECEIVED | | |
| 15V-Barrel 1 | 412° | 7.66 |
| 15V-Barrel 2 | 420° | 7.48 |
| HOPPERS | 480° | 6.15 |
| ● HEAT TREAT @ 405°C W/O AGITATION | | |
| 15V-12 hrs. | 472° | 6.85 |
| -14 hrs. | 490° | 7.13 |
| -14.5 hrs.* | 495° | 7.36 |
| -16 hrs. | 495° | 7.93 |
| -18 hrs. | 480°-495° | 6.60 |
| -20 hrs. | 490°-505° | 6.87 |
| -20+cool+2 hrs. | 488° | 7.26 |
| ● HEAT TREAT @ 405°C WITH AGITATION | | |
| 15V-14 hrs. | 495° | 5.06 |

*Batch cooled then rapidly returned to 405°C

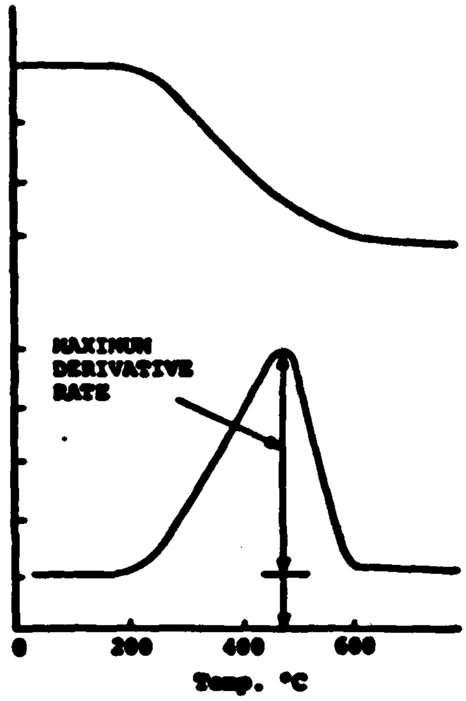


Figure 1-1. Maximum Decomposition Rates and Temperatures

| MATRIX/CONDITION | REMAINING WEIGHT (%) 600°C | 1000°C |
|---|---|---|
| ● AS RECEIVED | | |
| 15V-Barrel 1 | 28.7 | 26.9 |
| 15V-Barrel 2 | 33.0 | 29.9 |
| HOPPERS | 41.7 | 39.9 |
| ● HEAT TREAT @ 405°C W/O AGITATION | | |
| 15V-12 hrs. | 37.9 | 35.1 |
| -14 hrs. | 37.6 | 35.5 |
| -14.5 hrs.* | 38.7 | 36.2 |
| -16 hrs. | 38.5 | 36.8 |
| -18 hrs. | 40.6 | 38.3 |
| -20 hrs. | 39.5 | 37.7 |
| -20+cool+2 hrs. | 40.3 | 38.5 |
| ● HEAT TREAT @ 405°C WITH AGITATION | | |
| 15V-14 hrs. | 49.7 | 47.2 |

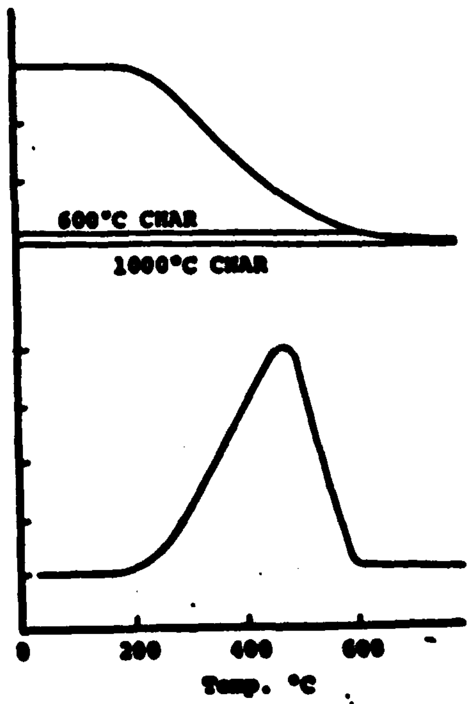


Figure 1-2. Comparative Weight Loss at 600°C and 1000°C

| MATRIX/CONDITION | TEMPERATURE, °C LOWER | UPPER | Δ |
|---|---|---|---|
| • **AS RECEIVED** | | | |
| 15V-Barrel 1 | 370° | 475° | 105° |
| 15V-Barrel 2 | 373° | 479° | 106° |
| HOPPERS | 385° | 510° | 125° |
| • **HEAT TREAT @ 405°C W/O AGITATION** | | | |
| 15V-12 hrs. | 394° | 498° | 104° |
| -14 hrs. | 408° | 505° | 97° |
| -14.5 hrs.* | 405° | 509° | 104° |
| -16 hrs. | 408° | 508° | 100° |
| -18 hrs. | 403° | 505° | 102° |
| -20 hrs. | 407° | 511° | 104° |
| -20+cool+2 hrs. | 397° | 502° | 105° |
| • **HEAT TREAT @ 405° WITH AGITATION** | | | |
| 15V-14 hrs. | 396° | 503° | 107° |

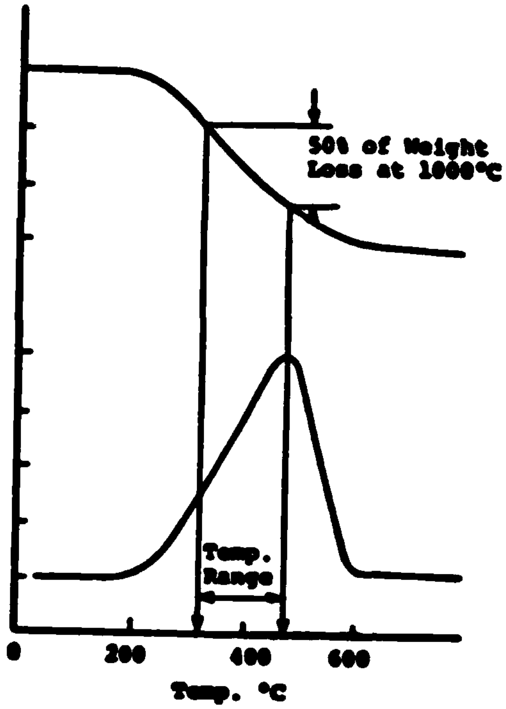


Figure 1-3. Median Temperature Range for Fifty Percent (50%) Weight Loss

| MATRIX/CONDITION | TEMP. RANGE °C | dy' $[10^{-4}(w/o).min^{-1}.°C^{-1}]$ |
|---|---|---|
| • **AS RECEIVED** | | |
| 15V-Barrel 1 | 316°-400° | 6.08 |
| 15V-Barrel 2 | 295°-405° | 5.30 |
| HOPPERS | 280°-465° | 2.53 |
| • **HEAT TREAT @ 405°C W/O AGITATION** | | |
| 15V-12 hrs. | 338°-454° | 3.93 Ave. |
| -14 hrs. | 350°-475° | 3.57 Ave. |
| -14.5 hrs.* | 340°-485° | 3.29 Ave. |
| -16 hrs. | 367°-490° | 3.79 Ave. |
| -18 hrs. | 330°-470° | 3.46 Ave. |
| -20 hrs. | 360°-493° | 3.63 Ave. |
| -20+cool+2 hrs. | 363°-480° | 3.65 |
| • **HEAT TREAT @ 405°C WITH AGITATION** | | |
| 15V-14 hrs. | 310°-460° | 2.44 Ave. |

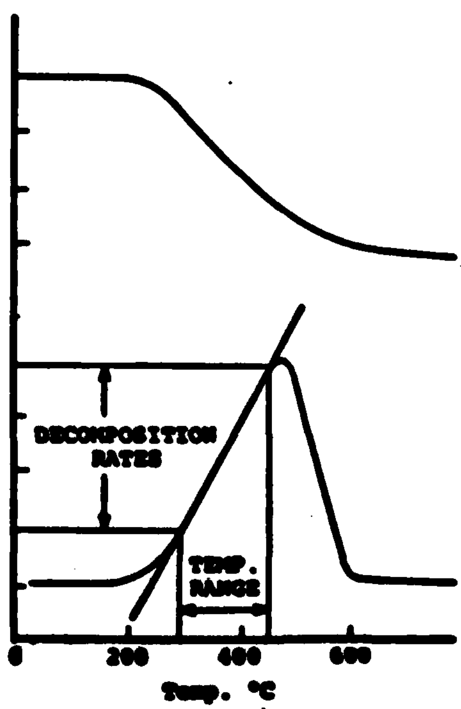


Figure 1-4. Derivative Rate of Change (dy') of Initial Decomposition

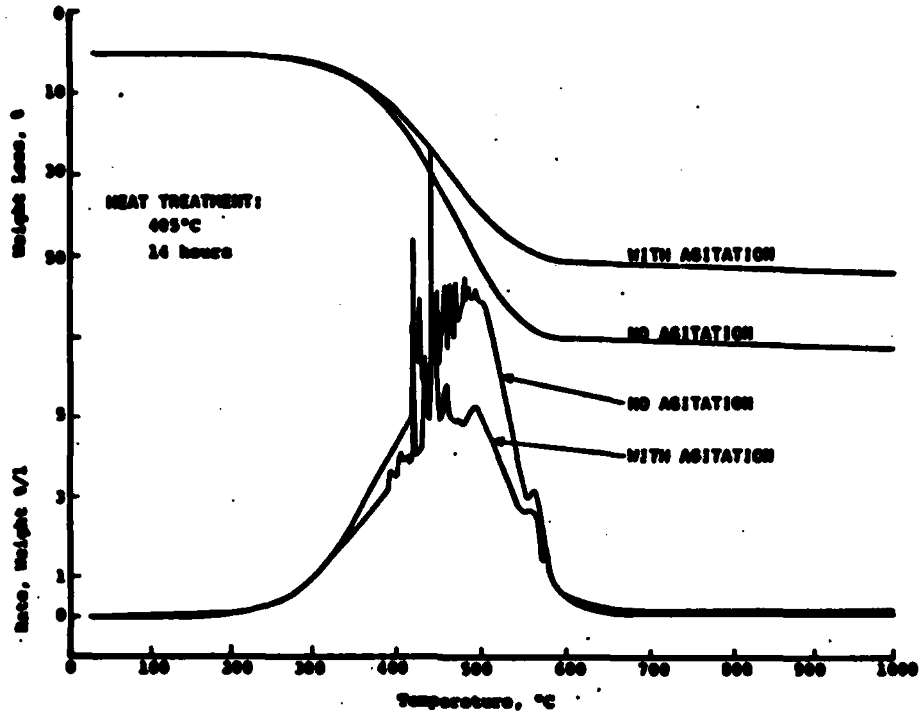


Figure 1-5. Effect of Mechanical Agitation on Weight Loss of Similarly Heat Treated Allied 15V Pitch (TGA Data)

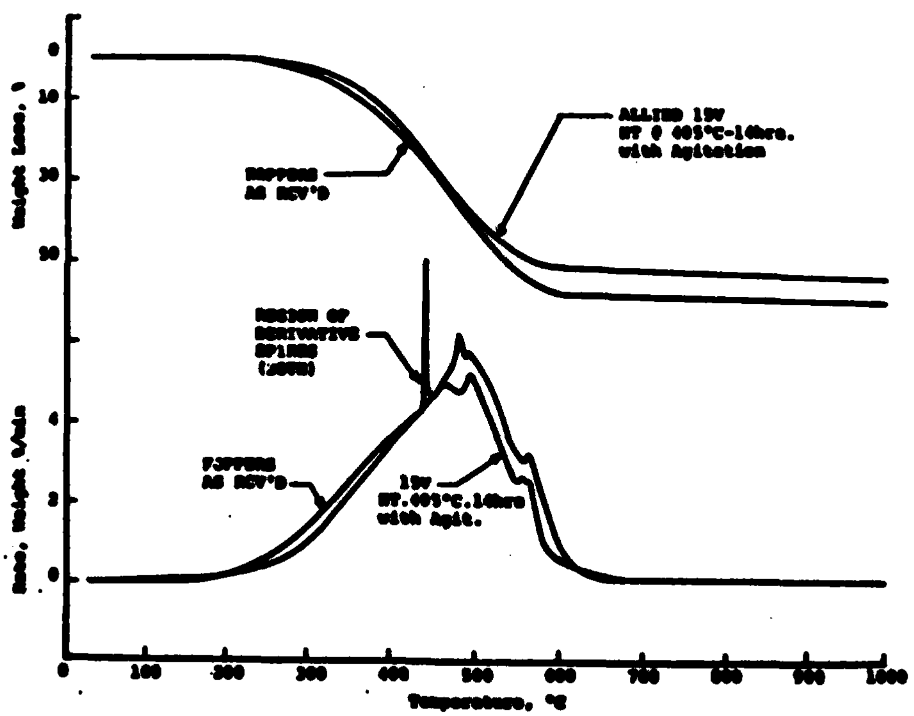


Figure 1-6. Weight Loss Similarity Between Mechanically Agitated and Heat Treated Allied 15V with "As Received" Koppers 15V (TGA Data)

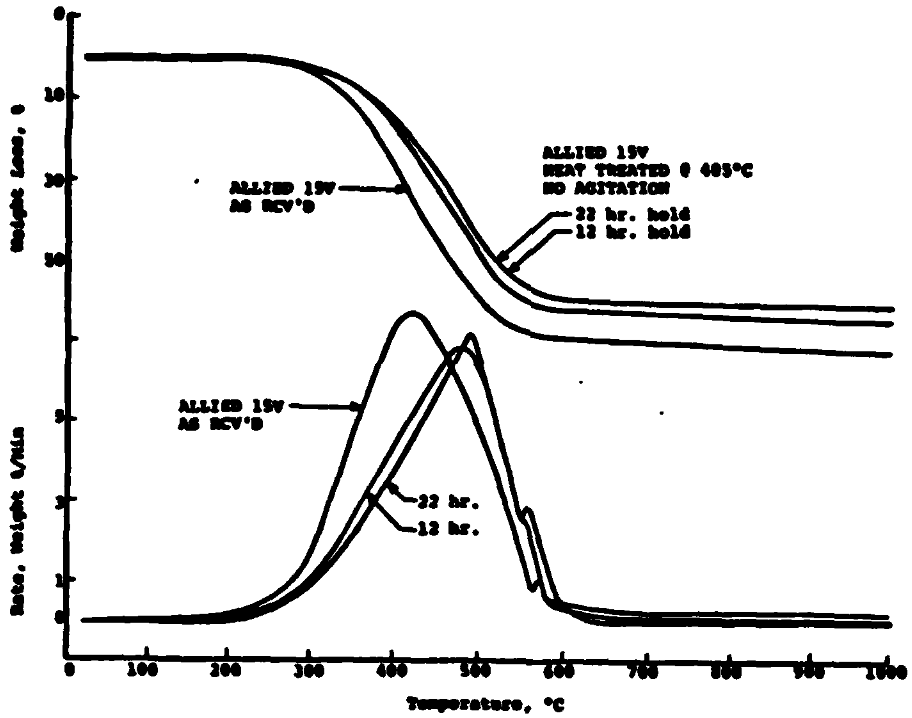


Figure 1-7. Effect of Heat Treatment Residence Time on Weight Loss of Allied 15V (TGA Data)

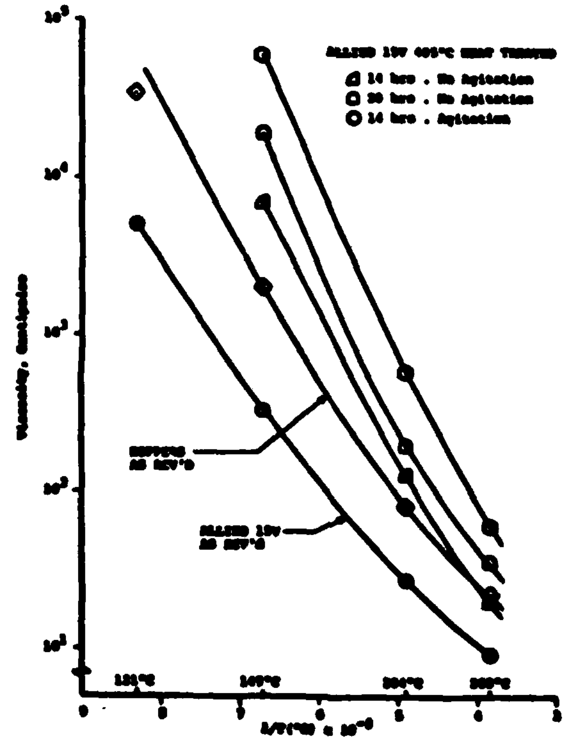


Figure 1-8. Viscosity of Allied 15V, Koppers 15V, and Heat Treated Allied 15V

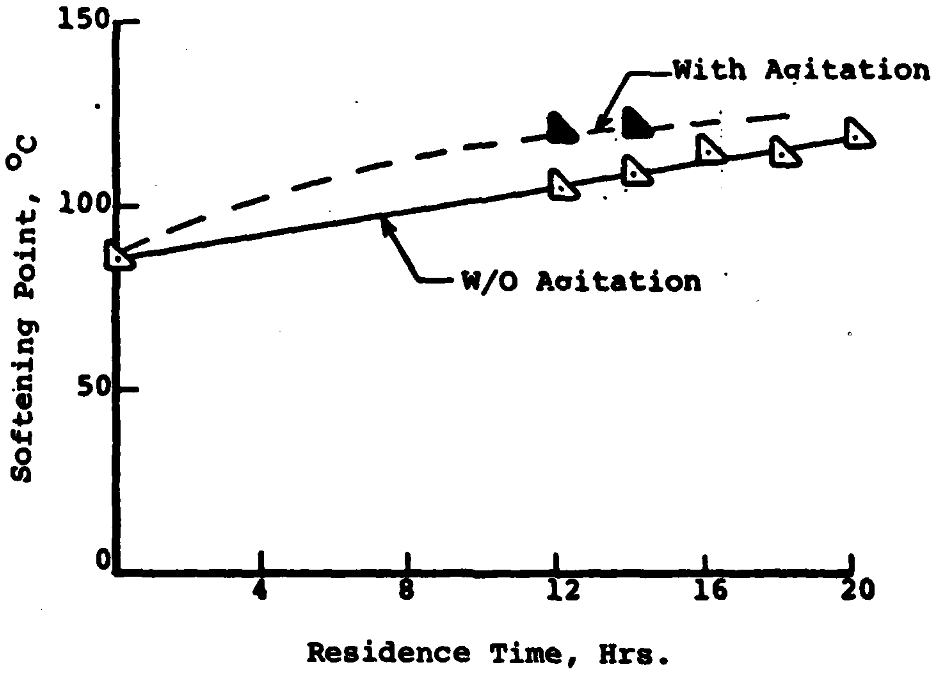


Figure 1-9. Softening Point of Heat Treated Allied 15V

# A P P E N D I X 2

## MESOPHASE FORMATION STUDIES

(Figures)

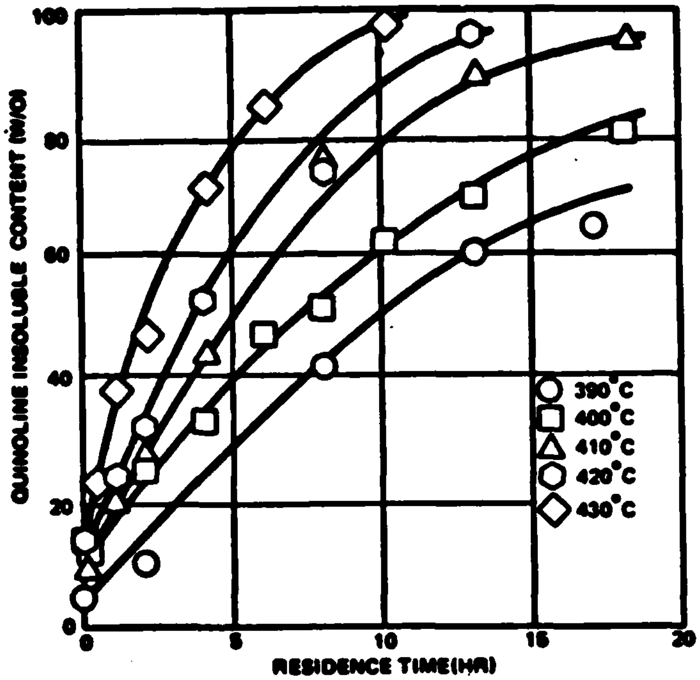


Figure 2-1. Mesophase Formation Rate (From Honda, H., Kimura, H., Sanada, Y., Sugawara, S. and Fusuta, T. Carbon, Vol. 8, 1970, p. 181)

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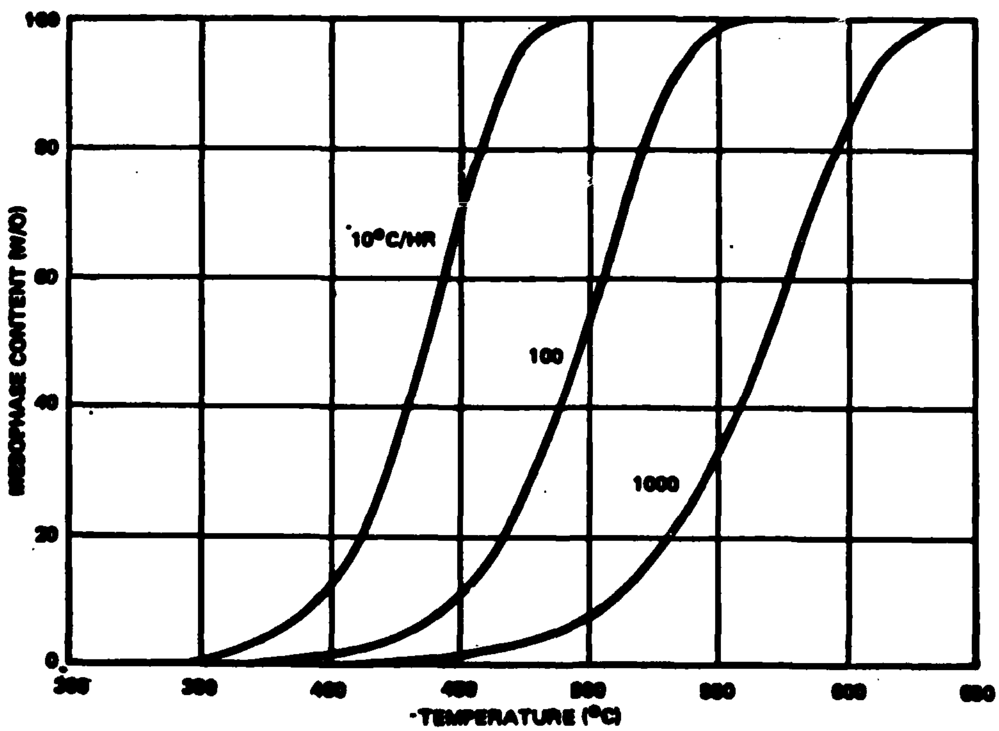
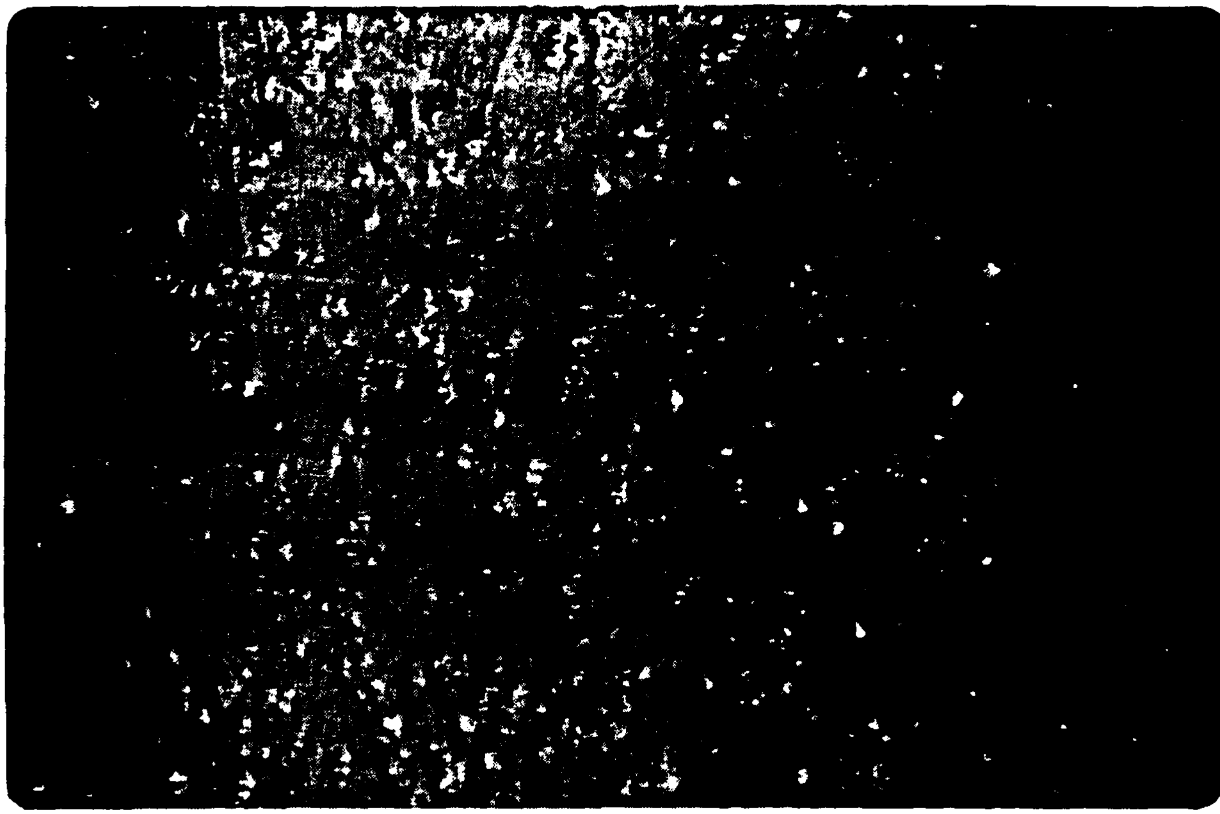


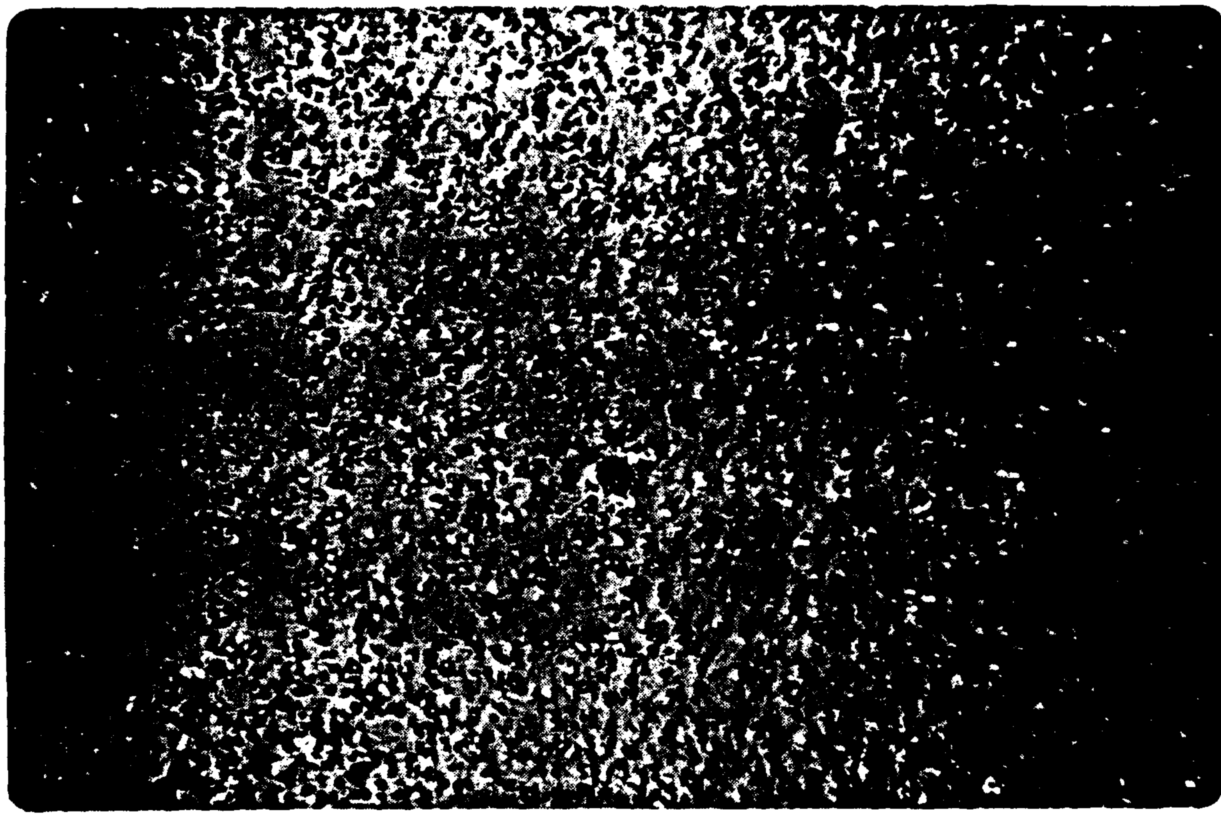

Figure 2-2. Mesophase Conversion for Constant Temperature Rise Rate (Calculated from Data in Figure 2-1)



500x

22 HOURS WITHOUT MECHANICAL AGITATION

FIGURE 2-3 EFFECT OF AGITATION (MIXING) OF HEAT TREATMENT (@ 405°C) CONDITIONING OF AS RECEIVED ALLIED 15V COAL TAR PITCH



80x

14 HOURS WITH MECHANICAL AGITATION

FIGURE 2-4 EFFECT OF AGITATION (MIXING) OF HEAT TREATMENT (@ 405°C) CONDITIONING OF AS RECEIVED ALLIED 15V COAL TAR PITCH

500x

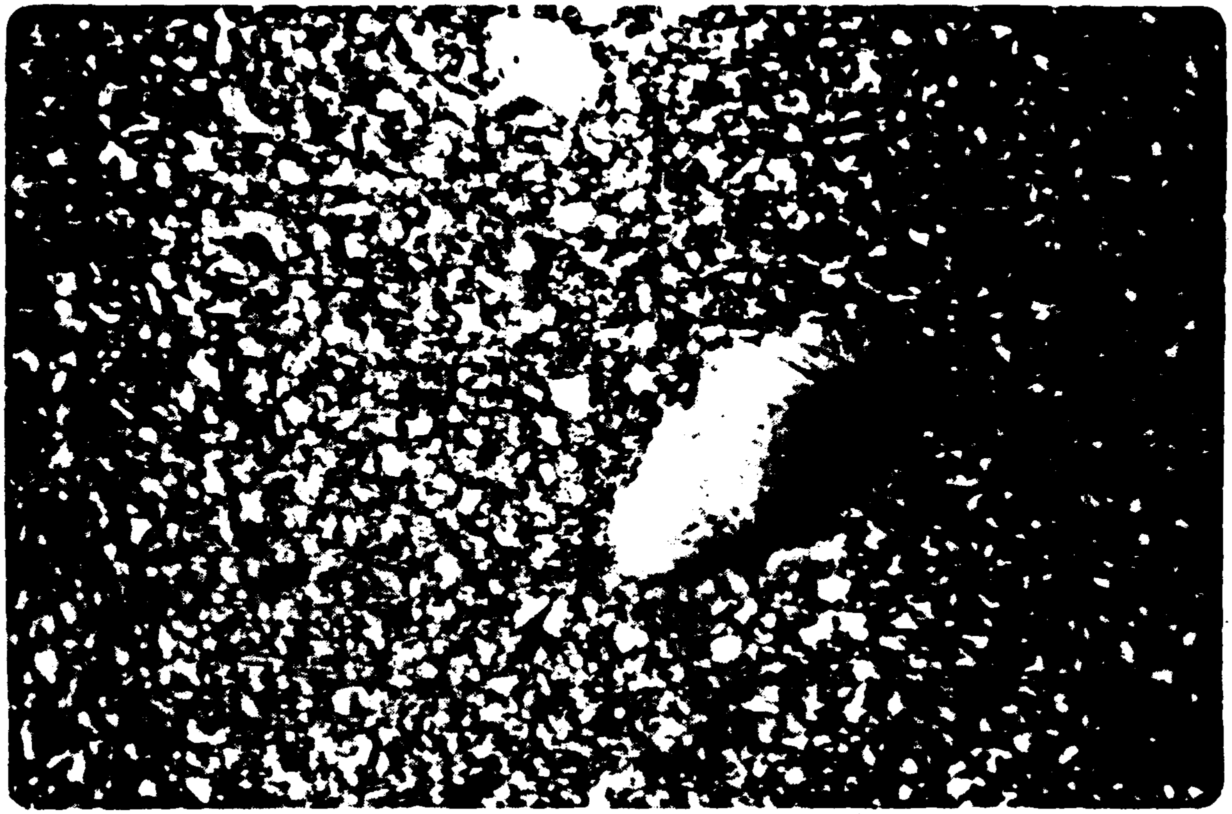
INTERRUPTED RUN-470°C/RAPID COOL

FIGURE 2-5 MESOPHASE COALESCENE DUE TO INTERRUPTED CYCLE AT 3000 PSI FOR ALLIED 15V COAL TAR PITCH

500x

FULL CARBONIZATION-615°C/HELD 4 HOURS

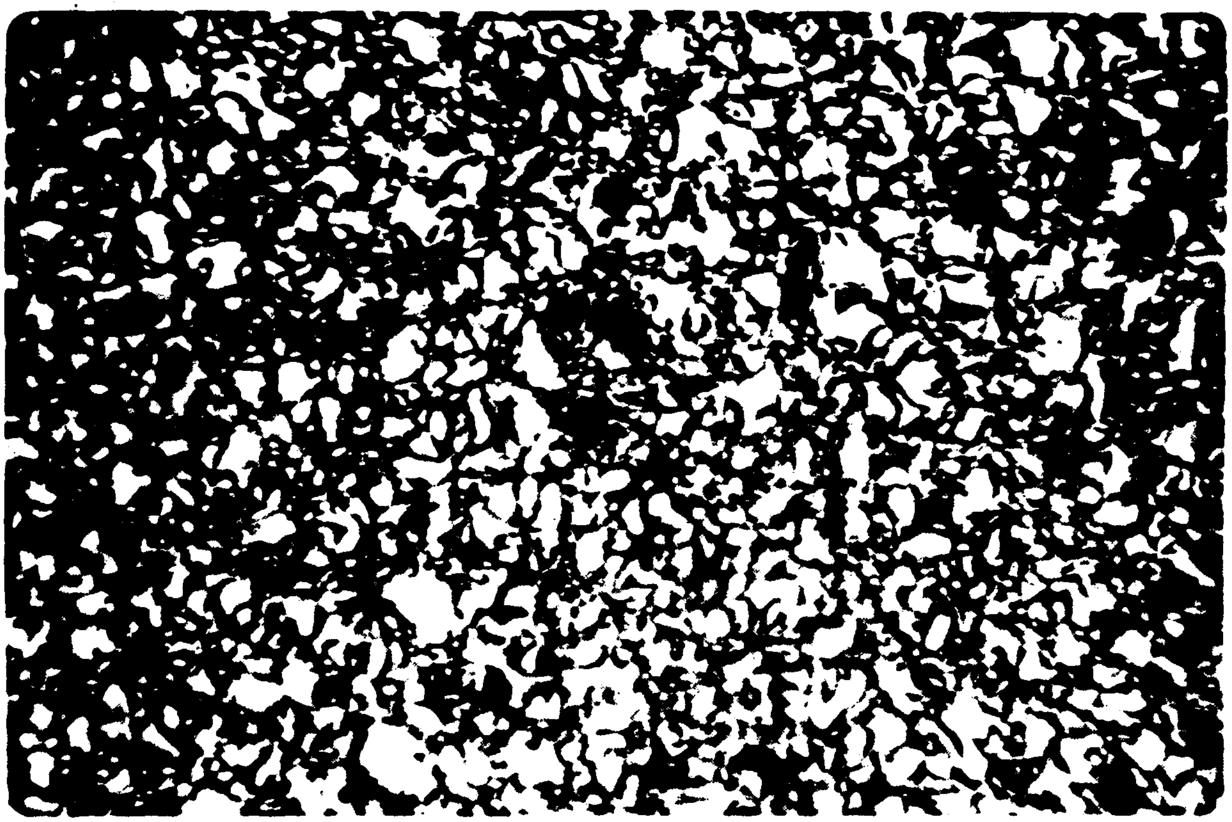
FIGURE 2-6 MESOPHASE COALESCENCE DUE TO FULL CARBONIZATION CYCLE



500x

INTERRUPTED RUN-470°C/RAPID COOL

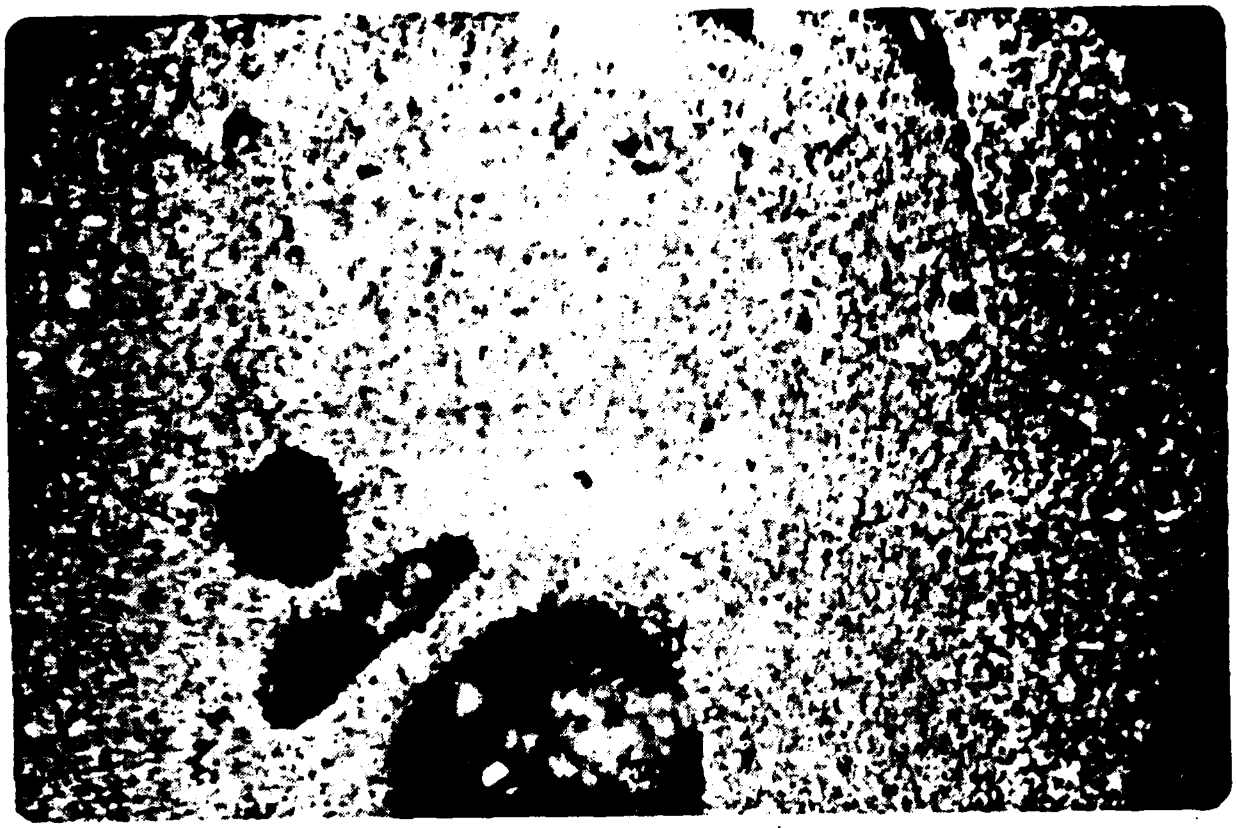
FIGURE 2-7 TYPICAL MESOPHASE PARTICULATE SIZE DUE TO DEGREE OF CARBONIZATION OF ALLIED 15V COAL TAR PITCH.



500x

FULL CARBONIZATION - 615°C/HELD 4 HOURS

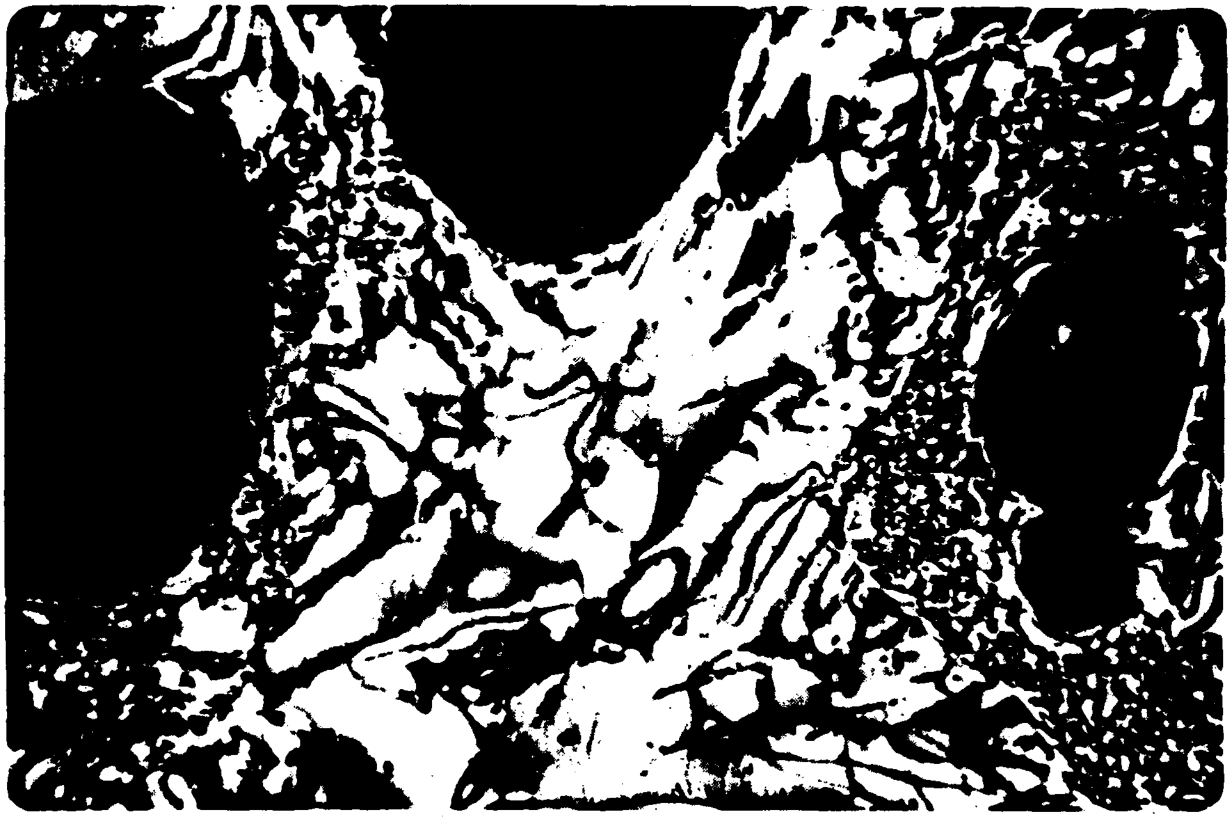
FIGURE 2-8 TYPICAL MESOPHASE PARTICULATE SIZE DUE TO DEGREE OF CARBONIZATION OF ALLIED 15V COAL TAR PITCH.



80x

INTERRUPTED RUN - 470°C / RAPID COOL

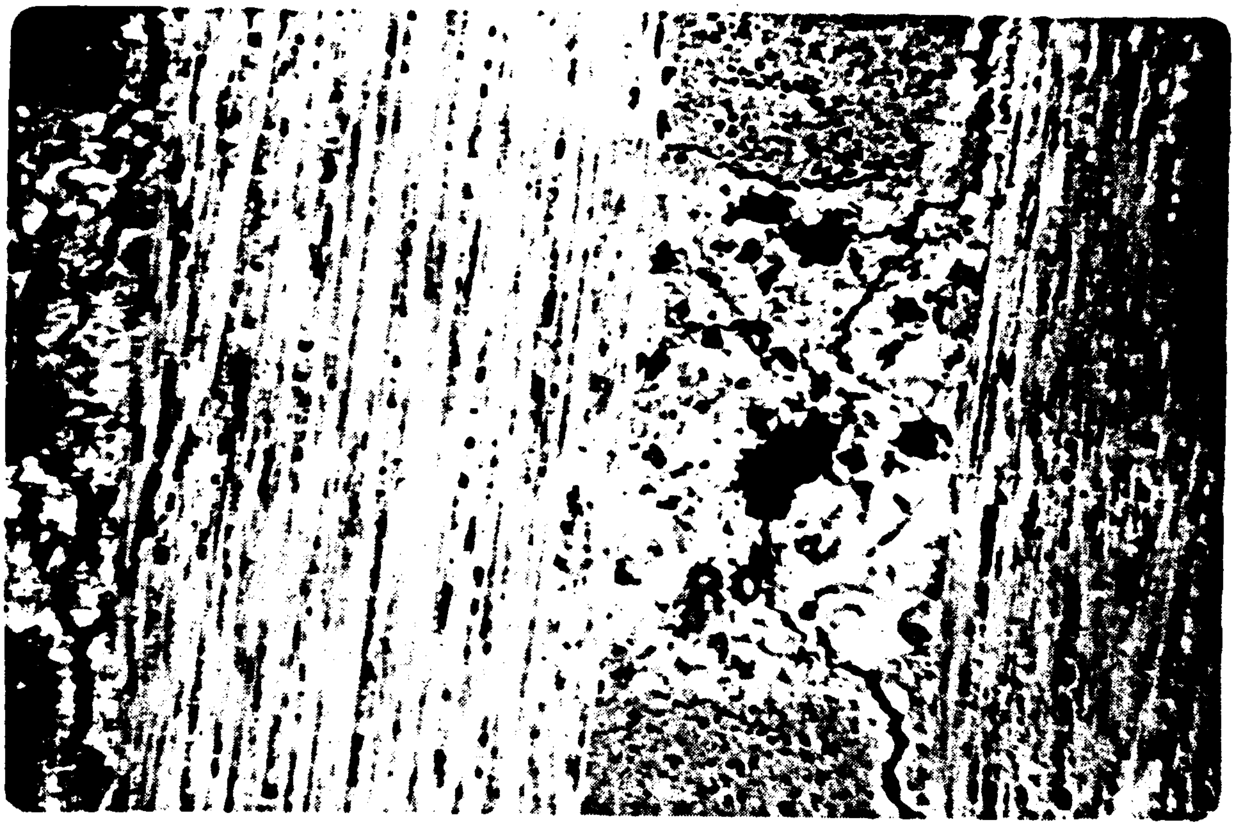
FIGURE 2-9 TYPICAL MESOPHASE / POROSITY INTERFACES SHOWING EFFECT OF GASEOUS PERCOLATION AND DEGREE OF CARBONIZATION AT 3000PSI FOR ALLIED 15V COAL TAR PITCH.



500x

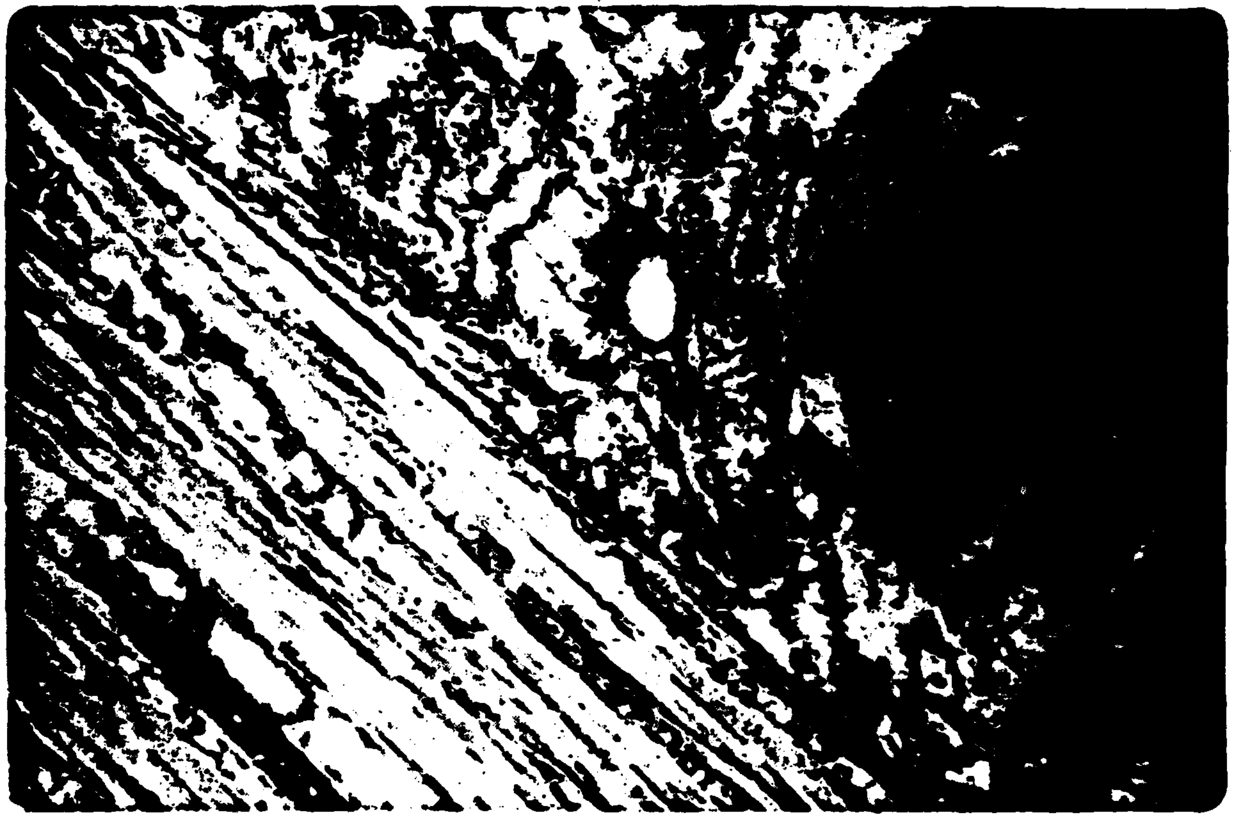
FULL CARBONIZATION - 615°C/HELD 4 HOURS

FIGURE 2-10 TYPICAL MESOPHASE/POROSITY INTERFACES SHOWING EFFECT OF GASEOUS PERCOLATION AND DEGREE OF CARBONIZATION AT 3000PSI FOR ALLIED 15V COAL TAR PITCH.



80x - FULL POL

FIGURE 2-11 MESOPHASE COALESCENCE IN GE 2-2-3, BILLET 408 R-2



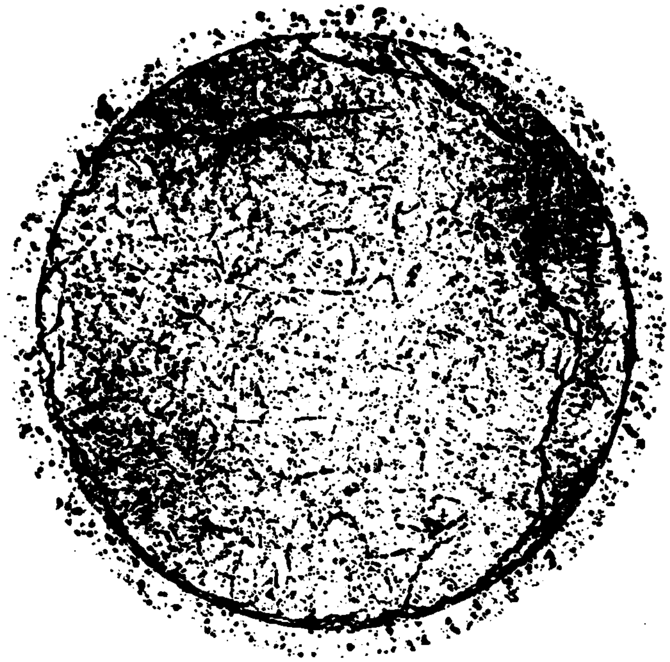
500x - POLARIZER ROTATED 15°

FIGURE 2-12 MESOPHASE COALESCENCE IN GE 2-2-3, BILLET 408 R-2 AT YARN/MATRIX INTERFACE

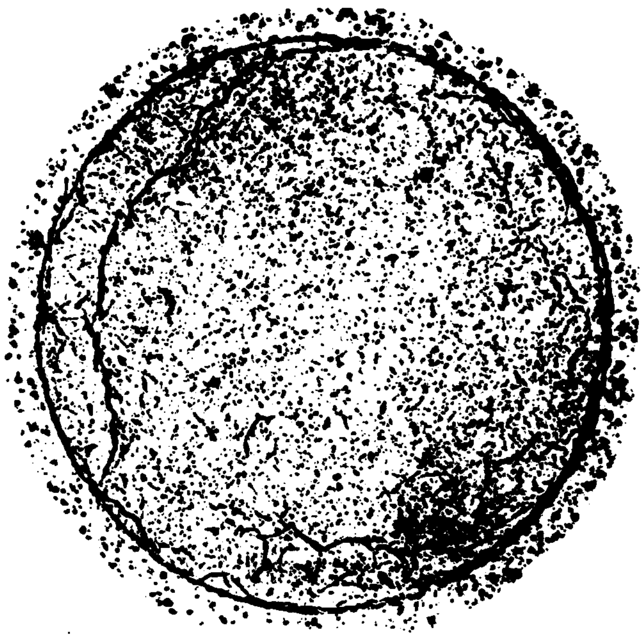
# APPENDIX 3

## FIBER/CARBONIZATION STUDIES

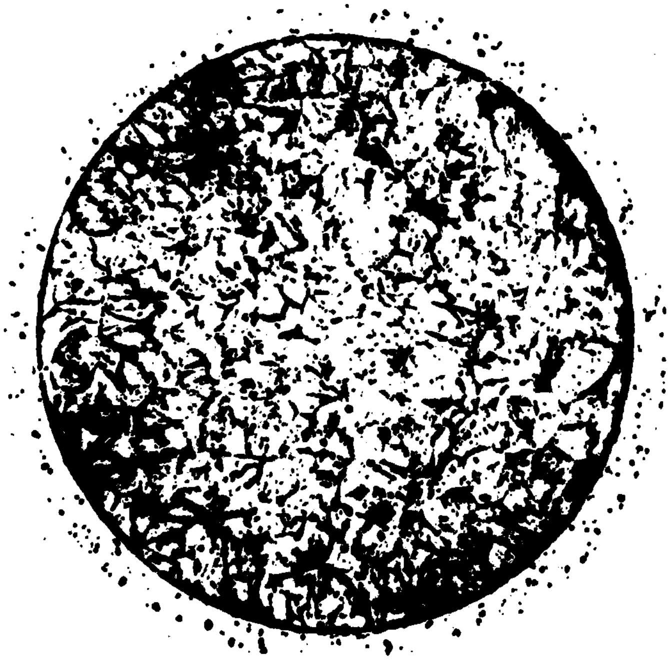
(Figures)



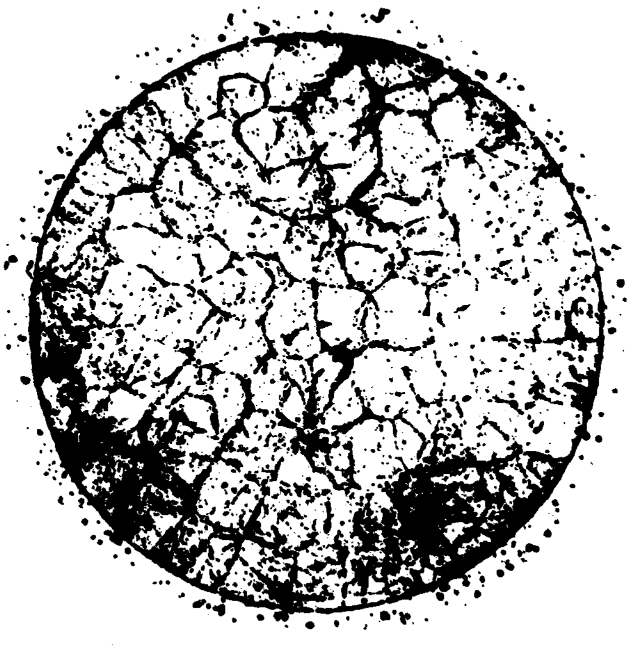
a. VSB-32 FULLY CARBONIZED



NM-10,000 FULLY CARBONIZED

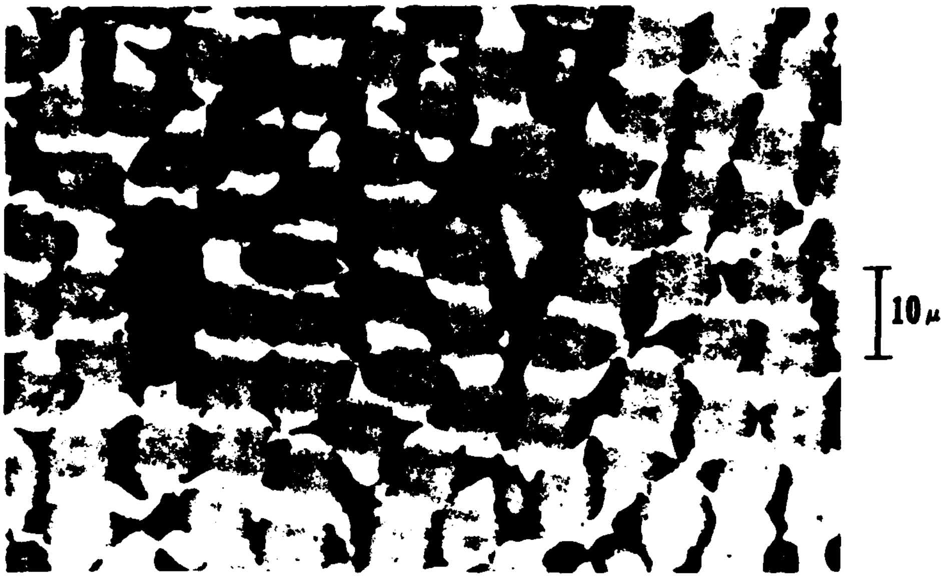


b. VSB-32 INTERRUPTED AT 470°C

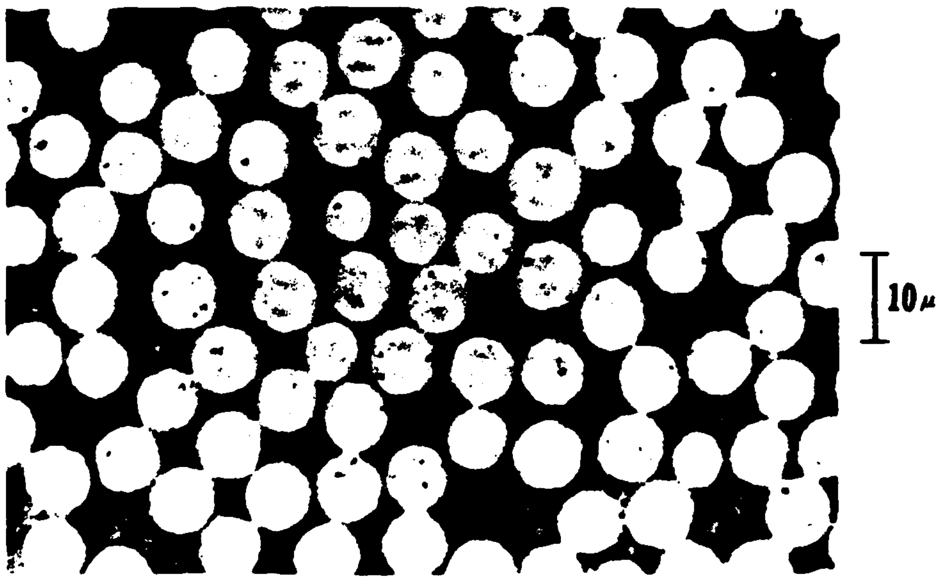


NM-10,000 INTERRUPTED AT 470°C

FIGURE 3-1 TRANSVERSE VIEW OF 70 YARN BUNDLE PACKS SHOWING RESTRUCTURING DUE TO DEGREE OF CARBONIZATION AT 10,000 PSI (10x)

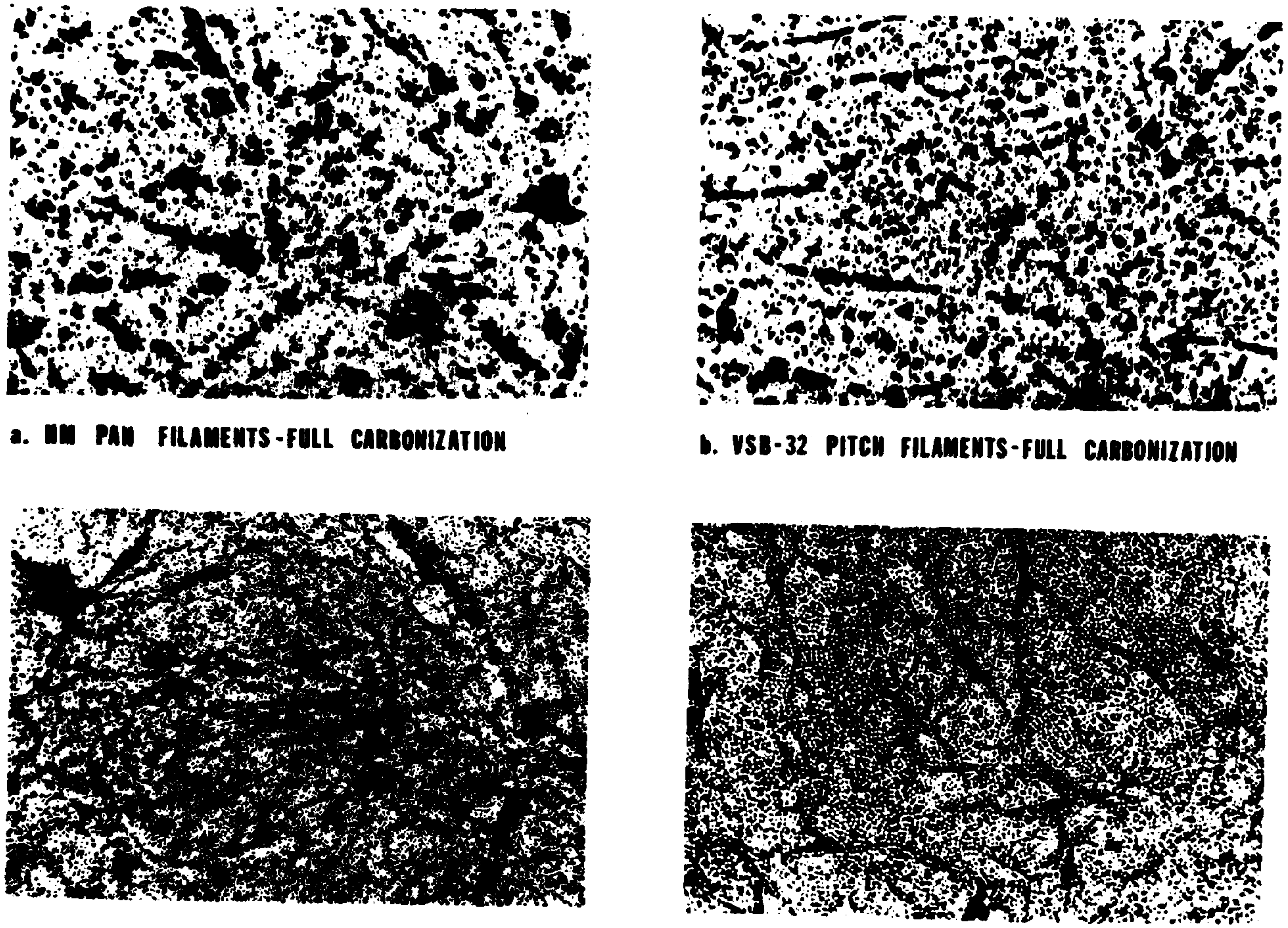



a. FULL CARBONIZATION CYCLE




b. INTERRUPTED CARBONIZATION CYCLE

FIGURE 3-2 COMPARISON OF FILAMENT SHAPE AT 470°C (INTERRUPTED CYCLE) AND 650°C (FULL CYCLE) IN 10,000 PSI CARBONIZATION AT 100°C/HOUR HM YARN



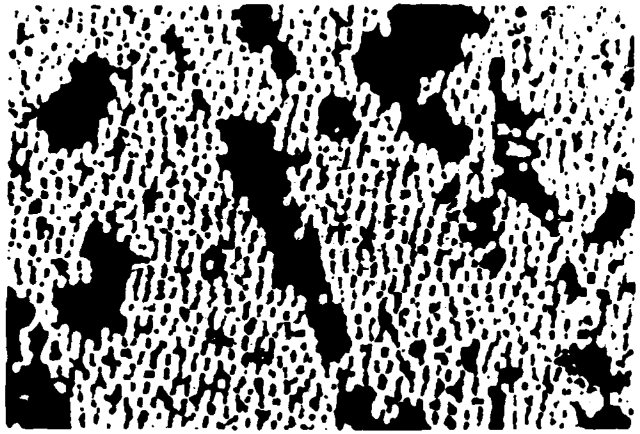
a. HM PAN FILAMENTS-FULL CARBONIZATION

b. VSB-32 PITCH FILAMENTS-FULL CARBONIZATION

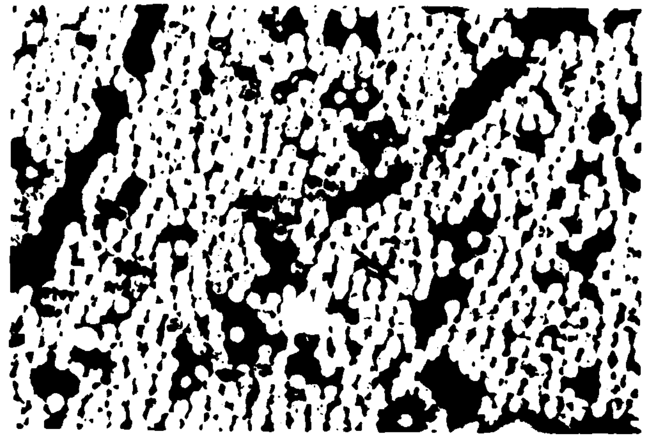
c. HM PAN FILAMENTS-INTERRUPTED CARBONIZATION

d. VSB-32 PITCH FILAMENTS-INTERRUPTED CARBONIZATION

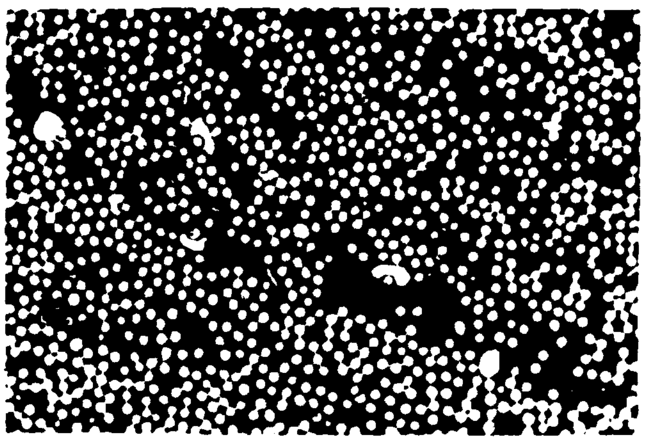
FIGURE 3-3 EFFECT OF DEGREE OF CARBONIZATION (AT 10,000 PSI AND 100°C/HOUR) ON HM PAN FILAMENTS AND VSB-32 PITCH FILAMENTS-90x



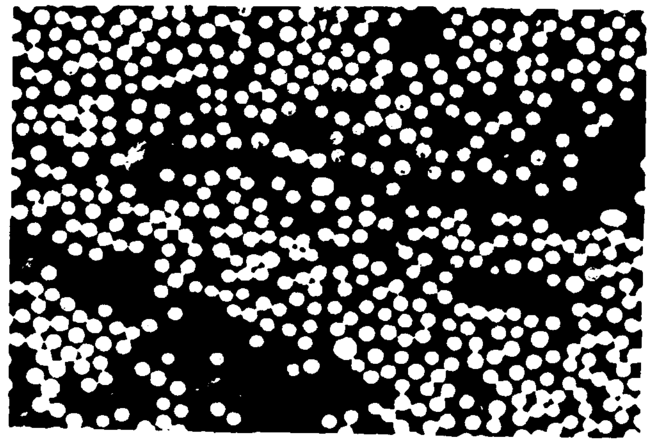
a. HM 10,000 PAN FILAMENTS-FULL CARBONIZATION



b. VSB-32 PITCH FILAMENTS-FULL CARBONIZATION

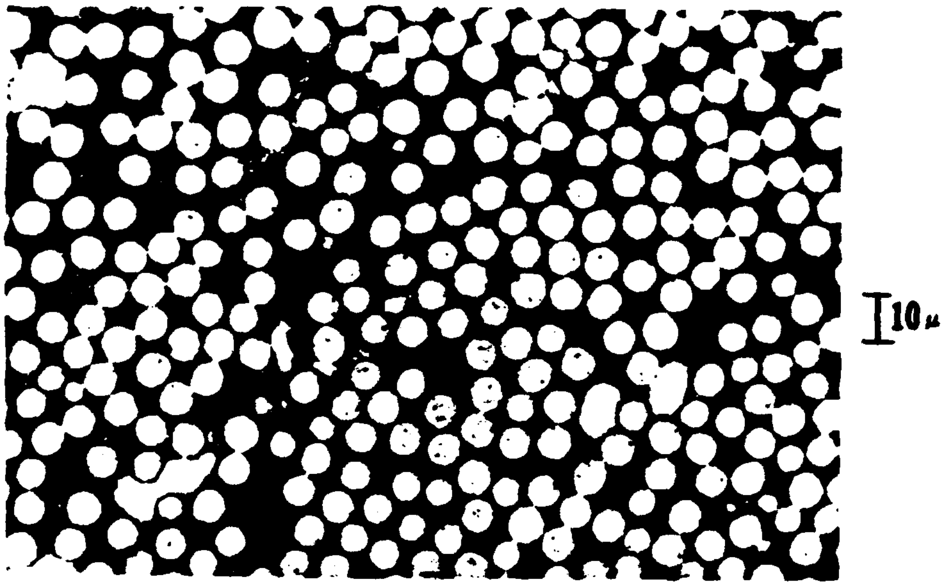


c. HM 10,000 PAN FILAMENTS-INTERRUPTED CARBONIZATION



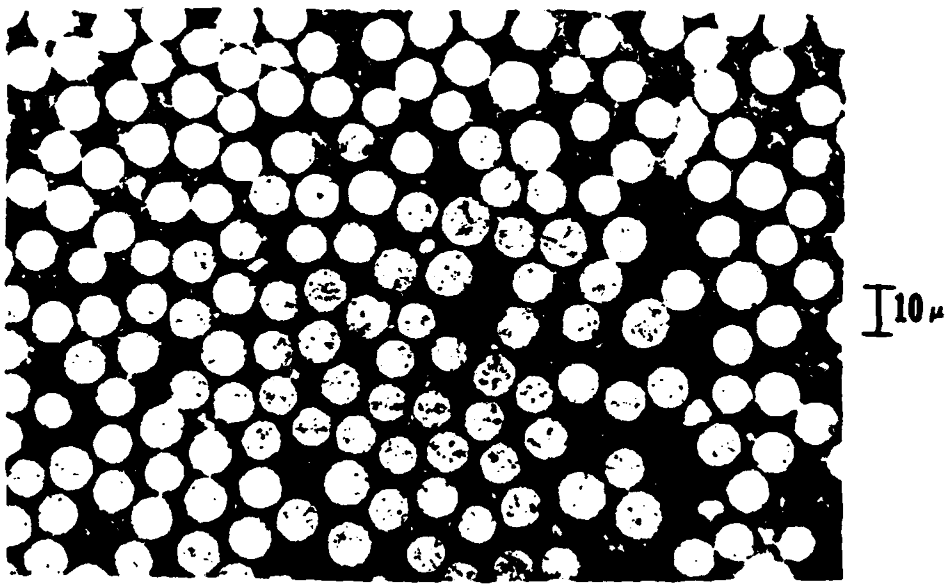
d. VSB-32 PITCH FILAMENTS-INTERRUPTED CARBONIZATION

FIGURE 3-4 RESTRUCTURING OF FILAMENT/YARN BUNDLE DUE TO DEGREE OF CARBONIZATION (AT 10,000 PSI AND 100°C/HOUR) FOR HM PAN FILAMENTS AND VSB-32 PITCH FILAMENTS-320x




640x

a. HM 10,000 PAN FILAMENTS




640x

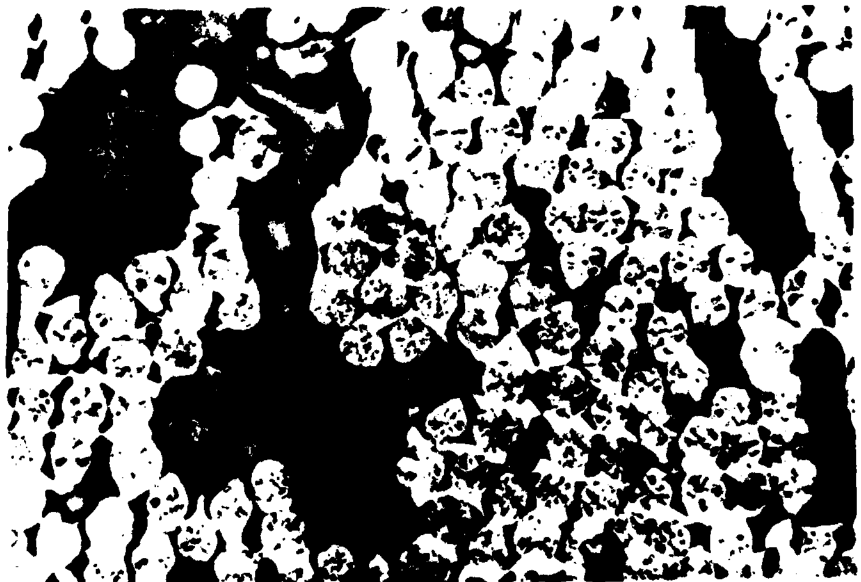
b. VSB-32 FILAMENTS

FIGURE 3-5 10,000 PSI CARBONIZATION HEAT RAMP INTERRUPTED AT 470° AND RAPIDLY COOLED.

10μ

640x

a. HM 10,000 PAN FILAMENTS



10μ

640x

b. VSB-32 FILAMENTS

FIGURE 3-6 10,000 PSI CARBONIZATION TO 650°C AT 100°C/HOUR HEAT RAMP